

# ADAPTATION OF THE AUGMENTED SPACE METHOD FOR THE COHERENT POTENTIAL AND CLUSTER COHERENT POTENTIAL APPROXIMATIONS FOR MAGNETIC ALLOYS

By  
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ADAPTATION OF THE AUGMENTED SPACE METHOD FOR  
THE COHERENT POTENTIAL AND CLUSTER COHERENT  
POTENTIAL APPROXIMATIONS FOR MAGNETIC ALLOYS

A Thesis Submitted  
in Partial Fulfilment of the Requirements  
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**ABUL KUMAR HESHA**

to the  
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CERTIFICATE

This is to certify that the work of this thesis entitled : ADAPTATION OF THE AUGMENTED SPACE METHOD FOR THE COHERENT POTENTIAL AND CLUSTER COHERENT POTENTIAL APPROXIMATIONS FOR KINETIC ALGEBRA has been carried out by ARUN KUMAR MISHRA under my supervision. No part of this work has been submitted elsewhere for a degree.

  
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*Abbas Khanna, Kolkata*

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## SYNOPSIS

This thesis entitled "ADAPTATION OF THE AUGMENTED SPACE METHOD FOR THE COHERENT POTENTIAL AND CLUSTER COHERENT POTENTIAL APPROXIMATIONS FOR MAGNETIC ALLOYS" submitted by Arun Kumar Mishra to the Department of Physics, Indian Institute of Technology, Kharpur in partial fulfillment of the requirements of the Ph.D. degree.

The problems of electronic states and electronic transport in disordered alloys are a matter of interest for a long time now both for theoretical and experimental physicists. For more than two decades now, the Coherent Potential approximation (CPA) remains one of the main tools in the hands of theoretical physicists working in the area of electronic structures of disordered alloys. In the simplest case of CPA calculation for random binary alloy  $A_xB_{1-x}$  where  $x$  is the concentration of A in B, the site energies are taken to be random (diagonal disorder) and the overlap integrals are assumed to be non-random i.e. there is no off-diagonal disorder. In this case correlated scattering from two or

more sites are ignored. Thus it is known as single site COHERENT POTENTIAL APPROXIMATION (SCPA).

The need to go beyond the single site was felt for a long time. In CHAPTER II, A self-consistent Cluster CPA formalism to obtain a configurationally averaged Green function is discussed. This formalism is based on AUGMENTED SPACE method introduced by Hoshino (1973). In the self-consistent cluster generalisation (CCPA) of SCPA, statistical clustering effects and off-diagonal disorder over finite cluster sizes are successfully taken into account. Besides, it preserves the Herglotz analytic properties of the Green function which is essential for getting physically meaningful results.

In all earlier applications of the Augmented Space approach the underlying potential was taken as known. In this chapter the Augmented Space approach is generalised to include cases where the potential itself has to be generated self-consistently. The work then involves two self-consistency loops - the one for generation of the Coherent Potential, given the random potential and then regeneration of the random potential itself. This generalisation is the principal contribution of the thesis.

The Augmented Space method coupled with the

Recursion method introduced by Haydock (1972) enables us to work on a realistic three-dimensional lattice. The Recursion method, discussed in CHAPTER III, is now a well established means of solving the Schrodinger equation for a system in which local interactions dominate. The local density of states and related quantities are calculated from the continued fraction expansions generated through the application of the recursion method. In this chapter the various terminator schemes have also been discussed. The density of states of pure Ni (the host in the system) is generated from the programme modified from the Cambridge Recursion Library (1984).

In chapter IV, an application of the above formalism is made. The electron correlation in narrow energy bands of transition metals is also dealt with. The system is Ni rich  $\text{Ni}_{1-x}\text{Fe}_x$  alloy in the magnetic states. The usual tight-binding Hamiltonian incorporates an extra term which accounts for the on-site Coulomb repulsion of the electrons. It is this term in the Hamiltonian which has to be generated self-consistently. This is the so called Anderson-Hubbard Hamiltonian which is used to consider the spin fluctuations and moment formation on alloying of the transition metal Ni with Fe. Another feature of this work is that, till now, the Augmented Space method was used only for the density of states calculations and other response

functions of the Green function like residual conductivity or optical conductivity etc. In this work local magnetisation is also considered, apart from the density of states calculations. The CPA and Cluster CPA results are obtained and compared. In low concentration regimes, i.e. the so called impurity regimes, the CPA fails to give good results, as in all earlier applications. The cluster generalisation gives correction in the right direction.

In Chapter V, the achievements and shortcomings of the present work is discussed. Some of the problems in the field is also suggested.

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## CHAPTER I

### INTRODUCTION

The problem of electronic states in disordered metallic alloys received the attention of solid state physicists with the application and extension of the pioneering work on the Coherent Potential Approximation (CPA) by Soven (1967), Kirkpatrick *et al.* (1970), Stocks *et al.* (1971) etc. Soven introduced the idea of a complex site energy (or potential) which characterizes the effect of the random environment within a meaningful picture. This potential (called the Coherent Potential) was determined self-consistently from the requirement that a particular configuration immersed in the effective medium (the mean field) yields no extra scattering on the average.

The validity of the single site CPA theory has been accepted in a large class of systems after its successful application to various model Hamiltonians suitable for disordered metallic alloys. Kirkpatrick *et al.* (1970) made its application to Ni-rich  $\text{Fe}_{1-x}\text{Cu}_x$  alloy and Stocks *et al.*

(1971) did the same for Cu rich  $\text{Cu}_{1-x}\text{Ni}_x$  alloys for studying the electronic density of states. Their results were in good agreement with the experimental data reported by Balb and Spicer (1966) and Buffum *et al* (1971).

Single site GF theory has, however, the following drawbacks:

- i) It takes into account only single site scattering and correlated scattering from clusters is not accounted for
- ii) the effect of potential fluctuations is suppressed while doing such an average
- iii) the off diagonal disorder in the tight-binding Hamiltonians cannot be properly accounted for

So the need was felt to go beyond the single site approximation and also incorporate off-diagonal disorder. Michel and Kruehnerl (1971) tried to make such a generalisation using a method based on the corrected cumulant expansion to find electronic density of states of an one-dimensional model of an alloy. Butler (1972, 1973) calculated the real and imaginary parts of the Green function using a self-consistent cluster method. Without going into the details of these methods, it will suffice to say that

both were attempts to improve the CPA by going beyond the single site approximation through making application to one-dimensional tight binding models. This generalization posed severe analytic problems, such as multivalued, discontinuous and negative density of states in certain energy regions.

Haydock et al (1973), Hockerman (1973 a,b), Muller-Hartman (1973) and Mills and Bakulaevskaya (1978) pointed out that for any real potential function, the Green function must obey certain mathematical properties called the Herglotz properties. A complex function  $f(z)$  was defined as Herglotz if

- i)  $\text{Im } f(z) \geq 0$  for  $\text{Im } z > 0$
- ii) Singularities of  $f(z)$  lie on the real axis, and
- iii)  $f(z) \rightarrow 0$  as  $|z| \rightarrow \infty$  (where  $z = E + i0^+$ )

In order to get physical results Herglotzicity has to be retained in any approximation to the Green function. The basic fault with a majority of the extensions of the CPA proposed in late 40's and early 70's was that they led to approximate Green functions which were not Herglotz. It has to be borne in mind that in the development of a theory which includes scattering from clusters, short ranged order,

off-diagonal disorder or the effects of positional disorder, Herglotz property must be inherently retained.

Some other attempts at generalisations led to the Molecular Coherent Potential approximation (MCPA) proposed by Taskade (1969) and Butler (1973), Embedded Cluster method (ECM) discussed by Imbrieffield (1981) and Maraff *et al* (1984) and Travelling Cluster approximation proposed by Mills (1975).

Huckebier (1971a, b, 1971 a,b,c) introduced a formalism called the augmented space formalism (ASF) to calculate configuration average of a general function of many random variables. He was able to incorporate scattering effects from statistically coupled sites in finite size clusters and also off-diagonal disorder in a self consistent manner.

Before understanding the Augmented Space method, we have to know what configuration averaging implies and why we need to configuration average a quantity ; as also what is it that we should average. In the study of disordered systems, configuration averaging is a necessary requirement. The potentials which describe a disordered solid are characterized by random parameters: random in space as in quenched disordered solids or random in time as in thermal disordered systems, for example, electrons in contact with a

phonon bath. There are examples where both spatial and temporal disorders are involved (for example, dirty alloys (Rohr) systems) at high temperatures. A particular realization of these parameters, either in a given sample or at an instant of time is what we refer to as the configuration of the system.

To understand why we must take resort to configurational averaging, we take an example, say of a crystalline, substitutionally random binary alloy, in which the regular lattice sites are randomly occupied by A or B type atoms. Cu-Ni is a good example. At  $T=0$ , the randomness is quenched and spatial, and may be described by a set of random occupation variables  $n_i$  which takes values 0 and 1 only and therefore determines, whether a site labelled by  $i$  is occupied by a A or a B type of atom. A configuration is determined by a particular assignment of 0's and 1's to the sequence  $\{n_i\}$ . Any one sample therefore corresponds to a particular configuration. There can be in all  $2^N$  different configurations for a sample containing  $N$  atoms. This is a very large number for macroscopic systems. When an experimentalist talks about the characteristics of the samples he measures, he wants average trends among his samples; he has no interest in the variations between the large number of configurations. If the fluctuations of a characteristic from sample to sample (i.e. from configuration

to configuration) is negligible compared to the mean, then it is the configuration average which should be compared with experimentally determined characteristics.

It is clear from above why configuration averaging is required. Also, it is the physically measured property which should be configurationally averaged: the density of states or the response functions rather than the Hamiltonian or self-energies; the diffusion probabilities rather than wave functions. Anderson (1969) has tried to explain some of the anomalous results on the nature of the spectrum of random tight binding Hamiltonians, which were proposed at that time, based on configuration averaging. That is why, Green function techniques are favoured for the study of disordered systems rather than the Schrödinger equation approach.

Configuration averaging is a valid procedure only when the probability distribution of the property under consideration is sufficiently well behaved so that the mean dominates over the higher moments. The intensity of over light transmitted through layered media with randomly varying refractive indices studied by Chandrosshkar (1970) and the closely related problem of the resistance of disordered chain is an example. Kumar and coworkers (1970, 1971) have shown that the variance of the resistance of a disordered chain diverges much faster than its mean as the length of the chain

increases. It is, therefore, not meaningful to talk in terms of the average resistance of a very long disordered chain.

Now something about spatial ergodicity. For a very large system, in the limit of infinite size, all possible environments may be achieved even in a single sample. The Fig 2.1 will illustrate this idea.

A global probe can sample all possible environments in the sample weighted with appropriate probabilities. A global property is thus automatically configurationally averaged, even if it refers to a single sample. Thus, a spatially global probe samples the entire configuration space just as in statistical mechanics, the entire phase space is sampled by a dynamically evolving system. Hence the name 'spatial ergodicity'. Such global properties need not be configurationally averaged all over again.

In § 2.2 in Chapter II, we will discuss in detail how to configurationally average any physical quantity in a simple tight binding model for a substitutionally disordered binary alloy. Response functions, like optical conductivity, residual resistivity etc. can be configurationally averaged.

Until now, the Augmented Space method has been used for parametrized Hamiltonians alone. For this it has come under criticism. The main aim of the present work is to



Fig. 1-1 Representation of different environments within a sample. For  $\delta = 0$ , all environments are realized.



extend Augmented Space Formalism to cases where the potential itself has to be found self-consistently. One such example is a system with a potential given by

$$V(\vec{r}) = V_{ex}(\vec{r}) + a \langle \rho(\vec{r}) \rangle^{-1/2} \quad (1.1)$$

where the second term is the exchange correlation potential with

$$\rho(\vec{r}) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \text{Im} \langle \psi(\vec{r}, \vec{r}, E) \rangle_{av} dE \quad (1.2)$$

$$\text{and } \langle \psi(\vec{r}, \vec{r}, E) \rangle_{av} = \langle \psi | H - E | \psi \rangle \quad (1.3)$$

Thus,  $\rho(\vec{r})$  can be evaluated self-consistently by the use of equations (1.2) and (1.3).

We shall, however, choose a simpler case, which is nevertheless of considerable interest. We shall study a magnetic alloy within the framework of the Hartree-Fock approximation. The spin dependent Hamiltonian is itself dependent on the number of up( $\uparrow$ ) or down ( $\downarrow$ ) electrons and hence has to be obtained self-consistently.

In Chapter II the Augmented Space Formalism is introduced with its mathematical formulations and it is shown how it can be used both for CPA and cluster CPA.

Chapter III deals with the Recursion method. It also incorporates the different terminator schemes and application to d-states. Chapter IV deals with electron correlation in narrow energy bands. It also discusses how the Hubbard model is utilized for the study of spin fluctuation and moment formation in Si rich  $\text{Ni}_{1-x}\text{Fe}_x$  systems for different Fe concentrations. Finally, magnetic moment results obtained theoretically are compared with the experimental results.

## CHAPTER II

### THE AUGMENTED SPACE METHOD

#### §.1 INTRODUCTION

An electron moving in a disordered solid experiences random potentials at the lattice positions. The Hamiltonian thus has a very large number of configurations. The disorder is characterized by a set of Hamiltonian parameters, which are random variables and, their joint probability distribution. The description of such systems, should be from a statistical point of view and the physical properties of the system may, for instance, be described through configuration averaging of the physical observables.

The Augmented Space Formalism (ASF) is a technique of configuration averaging where configuration fluctuations are systematically taken into account. The formalism is formally exact but, for practical calculations, approximations preserving constraints of physical origin may be generated. The ASF was first introduced by Nohakjee

(1972a,1973b) and later on Kaplan and Gray (1975,1977) provided a detailed exposition. It has been successfully utilized for averaging quantities like one particle Green functions and response functions related to two particle Green functions, particularly when we have to go beyond the single site approximations (i.e beyond the CPA) and have to include interesting effects, large off-diagonal disorder, short range order etc.

Previously, the formulations utilizing the AGF concentrated on model or parametrized Hamiltonians. The density functional approach leads to Hamiltonians self consistently derived from the particle density. The aim of this work is to develop such a formalism and apply it to magnetic systems like Fe rich Fe-Fe alloys.

### 3.2 MATHEMATICAL FORMULATION OF AGF AND ITS APPLICATION TO MODEL SYSTEMS

In his various communications Heckerisse (1973 a,b, 1975 a,b,c) has worked out the detailed mathematics of the AGF. Here we discuss the main points of the formalism. Our formulation will be in a tight binding basis.

In a substitutional system the lattice sites are

randomly occupied by the atoms of the type say A,B,C etc. In a binary alloy the site energy  $\epsilon_i$  is a random variable which takes values  $\epsilon_A$  or  $\epsilon_B$  depending upon whether the site is occupied by an A or B type of atom respectively. The Hamiltonian involves a random occupation variable  $n_i$  defined to take the value 0 or 1 according to the occupation of site  $i$  by an A or B type of atom. A set of values taken up by the random occupation variable  $\{n_i\}$  is called a *configuration*. Assuming no correlation between these random variables, we can define their distribution function in the form

$$P(\{n_i\}) = \prod_i p_i(n_i) \quad (2.1)$$

where  $p_i(n_i)$  is the probability density of the individual variables. This assumption ignores short range order due to chemical clustering effects. Kaplan and Gray (1981) have considered the more general case of such dependent variables within a Markovian short ranged order model.

Haydock (1972) suggested that the probability density  $p_i(n_i)$  satisfies  $p_i(n_i) \geq 0$  and  $\int p_i(n_i) dn_i = 1$ . Thus the probability density  $p_i(n_i)$  shares with the density of states, the property of positive definiteness and integrability. Physically too, both give the number (or fraction) of states in a range  $\delta\epsilon$  around the energy value  $\epsilon$ .

Wickhamjee (1973) introduced a hypothetical space  $\Phi$ , corresponding to a random variable  $n_i$  such that a basis set  $\{|f_n^i\rangle\}$  and an operator  $H^{(i)}$  on it characterized the random distribution of  $n_i$  through the relation

$$p(n_i) = -1/\ln 2 \ln \left\langle f_n^i \left| \left[ (n_i + \frac{1}{2}) I - H^{(i)} \right]^{-1} \right| f_n^i \right\rangle \quad (2.2)$$

Thus the quantities  $|f_n^i\rangle$ ,  $H^{(i)}$  and  $p(n_i)$  are respectively analogous to eigen vectors, Hamiltonian and density of states. Subsequently Wickhamjee (1973) described  $|f_n^i\rangle$  as the disorder field in analogy with a fermion/boson field and was able to give a diagrammatic representation of it in a way similar to Feynman diagrams for fermions or bosons. Knowing the Hamiltonian, it is straightforward to find the density of states; however, in our case we have the reverse problem at hand - for a given probability distribution we have to find out an operator  $H^{(i)}$  corresponding to  $p(n_i)$  such that equation (2.2) is satisfied. Here  $|f_n^i\rangle$  is a specially chosen member of the orthonormal basis  $\{|f_n^i\rangle\}$  in  $\Phi$ .

The problem can be handled in a way analogous to the continued fraction expansion of Green functions in the Recursive method (Havdick, 1972). One has to try to write the probability density  $p(n_i)$  in the form of a convergent

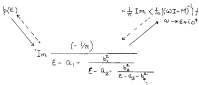


Fig. 2.1 Representation of three mathematical forms of positive, definite, integrable density function with finite moment.



Fig. 2.2 Representation of a renormalized vertices.

continued fraction (i.e. one has to follow the path shown in figure 2.1 by full lines) of the form as shown below :

$$p(z) = \lim_{n \rightarrow \infty} \frac{(1, n)}{z + i\eta - a_0 - \frac{b_1^2}{z + i\eta - a_1 - \frac{b_2^2}{z + i\eta - a_2 - \frac{b_3^2}{\ddots}}}} \quad (2.3)$$

such an expansion is convergent only if all the moments of  $p(z)$  are finite.

Having written the probability density in the above form the representation of the operator  $H^D$  in some basis  $|f_n\rangle$  can be written as a tridiagonal matrix with  $a_0, a_1, a_2, \dots$  etc along the diagonal and  $b_1, b_2, b_3, \dots$  etc along the off diagonal positions. It should be noted that for several distributions (like the Lorentzian), one cannot get a convergent continued fraction expansion. The whole thing breaks down as the moments of order  $> 2$  are divergent.

Let us choose our system to be a random alloy  $A_n B_{1-n}$  having only the diagonal disorder and nearest neighbour overlap only. Is the tight binding Anderson Hamiltonian



$$H = \sum_i \epsilon_i P_i + \sum_{i,j} \epsilon_{ij} \nabla T_{ij} \quad (2.4)$$

Here the diagonal terms  $\epsilon_i$  form a set of random variables. In terms of the random occupation variables

$$\epsilon_i = \epsilon_a n_i + \epsilon_b (1-n_i) \quad (2.5)$$

The off diagonal term  $\nabla$ , however, is not random.

$P_i = |i\rangle\langle i|$  is the Projection operator and  $T_{ij} = |i\rangle\langle j|$  is the transfer operator in the space  $\mathcal{H}$  spanned by the tight-binding basis  $\{|i\rangle\}$ .

Neglecting short range ordering, the probability density for the  $\{\epsilon_i\}$  is given by

$$p(\epsilon_i) = \alpha \delta(\epsilon_i - 1) + (1-\alpha) \delta(\epsilon_i)$$

$$= -(1/\pi) \operatorname{Im} \left[ \frac{\alpha}{\epsilon_i + i0^+ - 1} + \frac{(1-\alpha)}{\epsilon_i + i0^+} \right] \quad (\text{where } \alpha \rightarrow 0^+)$$

$$= -(1/\pi) \operatorname{Im} \left[ \frac{\alpha}{\epsilon_i - 1} + \frac{(1-\alpha)}{\epsilon_i} \right] \quad (\text{Where } \epsilon_i = \epsilon_i + i0^+)$$

$$= -(1/\pi) \operatorname{Im} \frac{1}{\epsilon_i - \alpha - \frac{\alpha(1-\alpha)}{\epsilon_i - (1-\alpha)}}$$

$$= -(1/\pi) \operatorname{Im} \frac{1}{R_1 - a_1 + b_1^2 / (R_1 - a_1)} \quad (2.8)$$

where  $a_1 = \alpha$ ;  $a_2 = (1-\alpha)$  and  $b_1^2 = \alpha(1-\alpha)$

Thus  $\mathbf{R}^{(1)}$  has  $2 \times 2$  tridiagonal matrix representation given by

$$\begin{bmatrix} \alpha & \sqrt{\alpha(1-\alpha)} \\ \sqrt{\alpha(1-\alpha)} & 1-\alpha \end{bmatrix} \quad (2.9)$$

in a basis  $\{|1_0^1\rangle, |1_1^1\rangle\}$  spanning the 'configuration space'  $\Phi_1$  of  $n_1$ .

Let us consider the probability distribution for a single variable  $n_1$  and the average of a function  $F(n_1)$

$$\begin{aligned} \bar{F} &= \int_{-\infty}^{\infty} F(n_1) P(n_1) \, dn_1 \\ &= - \int_{-\infty}^{\infty} F(n_1) (1/\pi) \operatorname{Im} g_{\alpha}^{(1)}(n_1) \, dn_1 \end{aligned} \quad (2.10)$$

where,  $R_1 = n_1 + i0^+$ ;  $g(R_1) = -(1/\pi) \operatorname{Im} \langle U_0 | g^{(1)}(R_1) | U_0 \rangle$ ;  
and  $g^{(1)}(R_1) = (R_1 I - H^{(1)})^{-1}$

Let us consider  $F(z)$  as a function of a complex variable  $z$  having no singularities on the real axis in the neighborhood of the branch cut of the function  $g_{\text{reg}}^{\text{M}}(z)$ . Then

$\bar{F} = - (1/2\pi i) \oint F(z) g_{\text{reg}}^{\text{M}}(z) dz$ ; where the contour is taken such that it goes round the branch cut of  $g_{\text{reg}}^{\text{M}}(z)$ .

$$z = (1/2\pi i) \oint F(z) dz \left\langle r_{\alpha} \left| \int_{-\infty}^{\infty} (z-h)^{-1} dp(h) \right| r_{\alpha} \right\rangle \quad (2.8)$$

where  $g^{\text{M}}(z) = \int_{-\infty}^{\infty} \frac{dp(h)}{z-h}$ ; and  $p(h)$  is spectral projection operator of  $\mathbf{H}^{\text{M}}$ .

$$\begin{aligned} \text{Thus, } \bar{F} &= \langle r_{\alpha}^{\dagger} | \int_{-\infty}^{\infty} F(h) dp(h) | r_{\alpha}^{\dagger} \rangle \\ &= \langle r_{\alpha}^{\dagger} | F(\mathbf{H}^{\text{M}}) | r_{\alpha}^{\dagger} \rangle \end{aligned} \quad (2.10)$$

where the operator  $F(\mathbf{H}^{\text{M}})$  is the same functional of  $\mathbf{H}^{\text{M}}$  as  $F$  is of  $z$ . Thus we see that, in general, the configuration average can be written as a particular element of the representation of an operator constructed from the operator related to the probability distribution.

If we wish to generalize the theorem to functions of several independent random variables we introduce the

configuration space  $\mathcal{R} = \Pi_{i=1}^N \mathcal{R}_i$  and  $\mathcal{R} = \{|\mathcal{R}^{(i)}\rangle\} = \mathcal{R}^{\mathcal{R}} \otimes \mathcal{R}^{\mathcal{R}} \subset \mathcal{H}_1$ . Then the average of the function  $F(|\mathcal{R}_1\rangle)$  is given by

$$\begin{aligned} \bar{F} &= \int_{\mathcal{R}} \int_{\mathcal{R}} |\mathcal{B}| \, d\mathbf{a}_1 \, F(|\mathbf{a}_1\rangle) \, P(|\mathbf{a}_1\rangle) \\ &= \langle \mathcal{E}_0 | F(|\mathcal{R}^{(1)}\rangle) | \mathcal{E}_0 \rangle \end{aligned} \quad (2.11)$$

The configuration space  $\mathcal{R} = \Pi_{i=1}^N \mathcal{R}_i$  is indexed by  $|\mathcal{E}_0\rangle = |\mathcal{E}_{\mathbf{a}_1}\rangle \equiv |\mathcal{E}_{\mathbf{a}_2}\rangle \equiv |\mathcal{E}_{\mathbf{a}_3}\rangle \dots$   $\mathbf{a}$  is a composite index  $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \dots, \mathbf{a}_N)$  taking  $2^N$  values, since each  $\mathcal{R}_i$  can take values 0 and 1.  $|\mathcal{E}_0\rangle = |\mathcal{E}_0^1\rangle \equiv |\mathcal{E}_0^2\rangle \equiv |\mathcal{E}_0^3\rangle \dots \equiv |\mathcal{E}_0^N\rangle$ .  $F(|\mathcal{R}^{(1)}\rangle)$  is the same operator function of  $|\mathcal{R}^{(1)}\rangle$  as  $F(|\mathbf{a}_1\rangle)$  was a function of  $|\mathbf{a}_1\rangle$ . This is the AUGMENTED SPACE THEOREM.

### 2.3 HAMILTONIAN IN ACF FOR BOTH DIAGONAL AND OFF-DIAGONAL RESONANCE

We will start with the tight binding multi-band Anderson Hamiltonian

$$H = \sum_{i,j} \sum_{\sigma} t_{ij\sigma} \, \mathbf{r}_{i\sigma} + \sum_{i,j} \sum_{\sigma,\sigma'} V_{ij\sigma\sigma'} \, \mathbf{r}_{i\sigma\sigma'} \quad (2.12)$$

$$\text{where, } \mathbf{r}_{i\sigma} = \sigma_{i\sigma}^{\uparrow} \, \mathbf{r}_i + \sigma_{i\sigma}^{\downarrow} \, (1-\mathbf{r}_i) \quad (2.12a)$$

where  $i$  and  $j$  are the site indices and  $m, n$  are band indices.

$$V_{i,m;j,n} = V_{nm}^{AA} a_i b_j + V_{nm}^{BB} (1-a_i) (1-b_j) \\ + V_{nm}^{AB} (a_i (1-b_j) + b_j (1-a_i)) \quad (2.12b)$$

Here,  $a_i$  and  $V_{i,m;j,n}$  represent respectively diagonal and off-diagonal disorder arising from site energy and hopping integrals for the constituents A and B.

$$\sin \alpha_i = c \delta(a_i - 1) + (1-c) \delta(a_i) \quad (2.13)$$

where,  $a_i \in 0, 1$

$$H = H_0 + \sum_i \sum_m x_m V_{i,m}^{AB} + \sum_{(i,j)} \sum_{m,n} V_{nm}^{AB} a_i b_j T_{i,m;j,n} \\ + \sum_{(i,j)} \sum_{m,n} V_{nm}^{BB} (a_i + b_j) T_{i,m;j,n} \quad (2.14)$$

where,  $x_m \equiv (x_A - x_B)$  :  $V_{nm}^{AB} = V_{nm}^{AA} + V_{nm}^{BB} + 2 V_{nm}^{AB}$

and  $V_{nm}^{BB} = V_{nm}^{AB} - V_{nm}^{AA}$

The  $H^\dagger$  for each value of  $a_i$  has a representation

$$\begin{bmatrix} c & \sqrt{c(1-c)} \\ \sqrt{c(1-c)} & 1-c \end{bmatrix} \quad (2.15)$$

in the basis  $|f_i^{\downarrow}\rangle, |f_i^{\uparrow}\rangle$  spanning  $\phi_i$ .

The *Augmented Space Theorem* then yields the Hamiltonian in the *Augmented space* as

$$\begin{aligned} \bar{H} = & H_0 \otimes I + \sum_{i,j} c_{ij} P_{i,j} \otimes H^{ij} \otimes I^{ij} \\ & + \sum_{i,j} \sum_{\alpha,\beta} V_{i\alpha,j\beta}^{\alpha\beta} T_{i\alpha,j\beta} \otimes H^{ij} \otimes H^{\alpha\beta} \otimes I^{\alpha\beta} \\ & + \sum_{i,j} \sum_{\alpha,\beta} V_{i\alpha,j\beta}^{\alpha\beta} T_{i\alpha,j\beta} \otimes (H^{ij} \otimes I^{ij} + H^{\alpha\beta} \otimes I^{\alpha\beta}) \end{aligned} \quad (2.16)$$

$$\bar{H} \in \mathcal{H} \otimes \mathcal{H}_1^{\otimes} \otimes \mathcal{H}_1$$

$I^{ij}, I^{\alpha\beta}$  in the above equation indicate identity operators in all subspaces  $\phi_i$  except those superscripted.

## 2.4. CPA THROUGH THE AUGMENTED SPACE FORMALISM

Let us recapitulate the basic ideas behind single site CP approximation. We shall discuss the effective medium approach to derive the CPA equation. The tight binding Hamiltonian for a single band has the following form

$$H = \sum_i \epsilon_i P_i + \sum_{ij} V_{ij} T_{ij} \quad (2.17a)$$

where  $\epsilon_i$  takes the values  $\epsilon_A$  or  $\epsilon_B$  for binary alloy.  $\epsilon_A$  and  $\epsilon_B$  are site energies corresponding to A and B atoms respectively.

Thus,

$$[-\hbar^2/2m + V_i^c]|\psi\rangle = \epsilon_i|\psi\rangle \quad (2.17a)$$

$V_i^c$  = crystal potential corresponding to the  $i^{\text{th}}$  site.

$$V_{ij} = \langle i| \sum V_i^c |j\rangle \quad (2.17b)$$

We now suppose that the Hamiltonian (2.17a) has only diagonal disorder i.e. only  $\epsilon_i$  is random. The underlying philosophy in a single site effective medium theory is that if any of the effective potentials  $V(i)$  (coherent potential) are replaced by an exact potential  $\epsilon_i$  there would be no wave scattering on the average. Mathematically it is equivalent to saying that average of the single site scattering t-matrix vanishes i.e.

$$t_i(\epsilon) = \frac{\epsilon - \epsilon_i - \Sigma(\epsilon)}{\epsilon - 1 - G\epsilon_i - \Sigma(\epsilon)G\epsilon_i} \\ \langle t_i(\epsilon) \rangle = 0$$

$$(2.18)$$

where,

$\Sigma(z)$  is the Coherent Potential. It is translationally symmetric, but a complex, energy dependent function.

$\langle G(z) \rangle$  is the configuration averaged diagonal element of the Green function for the alloy, which, by definition is the Green function for the Coherent potential.

$$\langle G(z) \rangle = G_0(z - \Sigma(z)) \quad (2.18)$$

Equation (2.18) together with Equation (2.16) constitutes the self-consistent equations in the single site CPA which has the following form :

$$\frac{c(x_A - \Sigma(z))}{1 - (x_A - \Sigma(z)) \langle G(z) \rangle} + \frac{(1-c)(x_B - \Sigma(z))}{1 - (x_B - \Sigma(z)) \langle G(z) \rangle} = 0 \quad (2.20)$$

The above equation can be written in a more convenient form as follows:

$$\Sigma(z) = \bar{\Sigma} + \frac{c(1-c)\langle G(z) \rangle (x_A - x_B)^2}{1 - [(1-2c)\delta + (c^2 - \Sigma(z)) \langle G(z) \rangle]} \quad (2.21)$$

where,  $\bar{\Sigma} = c x_A + (1-c) x_B$  ;  $\delta = (x_A - x_B)$

We will now derive the same result via the Augmented Space formalism, in order to demonstrate the



equivalence of the two approaches.

We take a one atom cluster, i.e.  $Q^{th}$  site as our 'cluster'.

By the Augmented Space theorem, we have

$$\langle Q_{ann} \rangle = \langle Q, t_Q | (aI - \tilde{H})^{-1} | Q, t_Q \rangle \quad (2.22)$$

Here  $\tilde{H}$  is the expanded (Augmented space) Hamiltonian (2.16).

The configuration space for a single site is of rank 2, having  $|t_a\rangle$  and  $|t_b\rangle$  as the basis. The representation of  $\tilde{H}^{(a)}$  is given by (2.15).

In operator form,

$$\begin{aligned} \tilde{H}^{(a)} = & a|t_a^{(a)}\rangle \langle t_a^{(a)}| + (1-a)|t_b^{(a)}\rangle \langle t_b^{(a)}| \\ & + \sqrt{a(1-a)} (|t_a^{(a)}\rangle \langle t_b^{(a)}| + |t_b^{(a)}\rangle \langle t_a^{(a)}|) \end{aligned}$$

We now partition the expanded Hamiltonian  $\tilde{H}$  into the space I spanned by  $|0t_Q\rangle$  and  $|0t_Q\rangle$  and space II by the rest of the medium which we will replace by the effective medium. We will need to evaluate the elements of  $\tilde{H}$  in the space I only.

We have,

$$H_a = \sum_{ij} t_{ij} P_{ij} + \sum_{ij} V_{ij} T_{ij}$$

$$= a_{\mathbf{a}} + \delta a \sum_i v_i \cdot \vec{P}_i + \sum_{i,j} v_{ij} \cdot \vec{T}_{ij} \quad (2.23)$$

where,  $\delta a = a_{\mathbf{a}} - a_{\mathbf{b}}$

$$\vec{H} = H_{\mathbf{a}} + (-\vec{T}_{\mathbf{a}} + \vec{P}) \cdot \vec{P}_{\mathbf{a}} \quad (2.24)$$

where,  $\vec{P} = (1-\alpha)\vec{P}_{\mathbf{a}} + \alpha \vec{P}_{\mathbf{b}}$

We shall first evaluate the matrix elements of  $\vec{H}$  in the space  $I$

$$\begin{aligned} \langle 0, \vec{r}_{\mathbf{a}} | \vec{H} | 0, \vec{r}_{\mathbf{a}} \rangle &= a_{\mathbf{a}} + \delta a \sum_i \langle 0, \vec{r}_{\mathbf{a}} | \left\{ |00\rangle \equiv \mathcal{H}^{(0)} \right\} | 0, \vec{r}_{\mathbf{a}} \rangle \\ &\quad + \sum_{i,j} v_{ij} \langle 0, \vec{r}_{\mathbf{a}} | \left\{ |00\rangle \equiv I \right\} | 0, \vec{r}_{\mathbf{a}} \rangle \\ &= a_{\mathbf{a}} + \delta a \sum_i \delta_{i\mathbf{a}} \langle I | \mathcal{H}^{(0)} | I \rangle \\ &\quad + \sum_{i,j} v_{ij} \delta_{i\mathbf{a}} \delta_{j\mathbf{a}} \langle I | I \rangle = \delta_{i\mathbf{a}} \delta_{j\mathbf{a}} = 0, \text{ for } i \neq j \\ &= a_{\mathbf{a}} + \delta a \langle I | \mathcal{H}^{(0)} | I \rangle \\ &= a_{\mathbf{a}} + \delta a \alpha = \bar{a}, \quad \text{where } \bar{a} = \alpha a_{\mathbf{a}} + (1-\alpha)a_{\mathbf{b}} \end{aligned}$$

$$\text{Then, } \langle 0, \vec{r}_{\mathbf{a}} | \vec{H} | 0, \vec{r}_{\mathbf{a}} \rangle = \bar{a} \quad (2.25a)$$

$$\begin{aligned} \langle 0, \vec{r}_{\mathbf{a}} | \vec{H} | 0, \vec{r}_{\mathbf{b}} \rangle &= a_{\mathbf{a}} + \delta a \sum_i \langle 0, \vec{r}_{\mathbf{a}} | \left\{ |00\rangle \equiv \mathcal{H}^{(0)} \right\} | 0, \vec{r}_{\mathbf{b}} \rangle \\ &\quad + \sum_{i,j} v_{ij} \langle 0, \vec{r}_{\mathbf{a}} | \left\{ |00\rangle \equiv I \right\} | 0, \vec{r}_{\mathbf{b}} \rangle \end{aligned}$$

$$\begin{aligned}
&= \langle x_{\theta} \rangle + \delta\alpha \sum_i \delta_{i,0} \langle x_i | \mathcal{H}^{(0)} | x_i \rangle \\
&\quad + \sum_{i,j} \mathcal{V}_{i,j} \delta_{i,0} \delta_{j,0} \langle x_i | x_j \rangle \\
&= \langle x_{\theta} \rangle + \delta\alpha (1-\alpha) = \bar{x} \quad (2.25b)
\end{aligned}$$

$$\begin{aligned}
\langle 0, x_{\theta} | \tilde{H} | 0, x_{\theta} \rangle &= \langle x_{\theta} | x_{\theta} | x_{\theta} \rangle + \delta\alpha \sum_i \langle 0, x_{\theta} | \left\{ |\downarrow\uparrow\downarrow\downarrow\rangle \otimes \mathcal{H}^{(0)} \right\} | 0, x_{\theta} \rangle \\
&\quad + \sum_{i,j} \mathcal{V}_{i,j} \langle 0, x_{\theta} | \left\{ |\downarrow\uparrow\downarrow\downarrow\rangle \otimes \mathbb{I} \right\} | 0, x_{\theta} \rangle \\
&= \delta\alpha \sum_i \delta_{i,0} \langle x_i | \mathcal{H}^{(0)} | x_i \rangle + \sum_{i,j} \mathcal{V}_{i,j} \delta_{i,0} \delta_{j,0} \langle x_i | x_j \rangle \\
&= \delta\alpha \langle x_{\theta} | \mathcal{H}^{(0)} | x_{\theta} \rangle = \delta\alpha \sqrt{2(1-2)} = 0 \quad (2.25c)
\end{aligned}$$

$$\text{Similarly, one can show } \langle 0x_{\theta} | \tilde{H} | 0x_{\theta} \rangle = 0 \quad (2.25d)$$

$$\begin{aligned}
\text{Now, } [\alpha\mathbb{I} - H]^{-1} &= [\alpha\mathbb{I} - H_{\theta} + (-\mathbb{I}_{\theta} + \tilde{\alpha}\mathcal{P}_{\theta})]^{-1} \\
&= [(\alpha\mathbb{I} - H_{\theta}) + (\tilde{\alpha} - \mathbb{I}_{\theta})\mathcal{P}_{\theta}]^{-1} \\
&= [\alpha\mathbb{I}]^{-1} + (\tilde{\alpha} - \mathbb{I}_{\theta})\mathcal{P}_{\theta}]^{-1} \\
&= [1 + (\tilde{\alpha} - \mathbb{I}_{\theta})(\alpha\mathbb{I})\mathcal{P}_{\theta}]^{-1} \alpha\mathbb{I}
\end{aligned}$$

$$\text{So, } G_{\theta\theta}^{-1} = \frac{\langle \mathcal{P}_{\theta\theta} \rangle}{1 - (\tilde{\alpha} - \mathbb{I}_{\theta}) \langle \mathcal{P}_{\theta\theta} \rangle} \quad (2.26)$$

Thus, we have

$$\begin{aligned} E_m &= \bar{E} + \eta \langle Q_{\text{eff}, -\text{eff}}^{\text{eff}} \rangle \\ &= \bar{E} + \frac{\eta(1-\eta) \langle (r_m - r_m)^2 \rangle \langle Q_{\text{eff}} \rangle}{(1-\eta) \langle -E_m \rangle \langle Q_{\text{eff}} \rangle} \end{aligned} \quad (2.27)$$

The above equation (2.27) is identical to the equation (2.23) when we substitute the value of  $\bar{E}$ . Thus we have been able to show that CPA results can be derived via the AIP.

### 2.2 CLUSTER CORRELATION POTENTIAL APPROXIMATION (CCPA) IN THE ADAPTED SPACE BY GRAPHICAL METHODS

We start from the configuration averaged Green function

$$G_{\text{config}}(z) = \langle r_1 = r_0 | (z\vec{I} - \vec{H})^{-1} | r_1 = r_0 \rangle \quad (2.28)$$

where  $|r_0\rangle = \vec{I} \otimes |r_0^0\rangle$

At this stage we shall digress to discuss a graphical method for the calculation of Green functions and related resolvents. The method was discussed in this connection first by Bardeen (1972). It is an attractive

alternative to the algebraic multiple scattering methods is that it clearly, visually illustrates some of the cumbersome algebraic expressions.

## 7.31 THE GRAPHICAL METHOD

By a graph we mean a set of vertices connected by links. Let  $\{|\phi\rangle\}$  be any complete linearly independent basis in which the Hamiltonian is described. The overlap matrix  $S_{ij} = \langle i|\phi\rangle$  is a unit matrix provided the basis is orthonormal. Matrix elements of an operator  $M$  are given by  $M_{ij} = \langle i|M|\phi\rangle$ . A graph is associated with every basis  $\{|\phi\rangle\}$ . To every element  $|\phi\rangle$  of the basis set  $\{|\phi\rangle\}$  is associated a vertex  $V_i$  and to each distinct pair of elements  $\{|\phi\rangle, |\phi'\rangle\}$  a link or bond  $l_{ij}$  which may be directional (i.e.  $l_{ij}$  may not be equal to  $l_{ji}$ ) or otherwise. To any operator  $M$  there corresponds a graph consisting of vertices and links for which  $M_{ij} = 0$ . If we want to invert an operator  $M$  then the association of each vertex  $V_i$  is defined as

$$E(V_i) = 1/M_{ii}$$

and that of the link  $l_{ij}$  as

$$E(l_{ij}) = M_{ij}$$

A path of length  $n$  is a sequence of vertices connected by  $n$  links

$$P_n = (V_1, V_2, V_3, \dots, V_n)$$

Contribution of a path of length  $n$  is given by

$$K(P_n) = \prod_{i=1}^{n-1} K(V_i, V_{i+1}) \quad (2.29)$$

The Green function  $G_{ij}(x) = \sum_{n=0}^{\infty} \sum_{P_n \in d_{ij}} K(P_n)$ , where  $d_{ij}$

is the set of all paths connecting the vertices  $V_i$  and  $V_j$ .

It is well known that the summation or even statistical estimation of all paths between two vertices on a general lattice is not a tractable problem. We therefore go through a renormalisation procedure.

Let us introduce the definition of a non-intersecting path  $P_n'$ . A path  $P_n' = (V_1, V_2, V_3, \dots, V_n)$  is non-intersecting if none of the internal vertices  $V_2, \dots, V_{n-1}$  are the same. If  $V_n = V_1$  then the path is a closed, or polygonal non-intersecting path.

We now gather together all paths starting from  $V_1$ , going through  $V_i$  to  $V_j$  either directly or via other vertices.

This renormalizes the vertices  $V_n$  (see figure (2.8)). If we do this for every vertex, we obtain at the end only non-intersecting paths but the contribution  $K(V_n)$  is renormalized to

$$K'(V_n) = Q_{ren}^{(1)A} \dots^{(n)A}(z) \quad (\text{Haydock 1972; Meekerjee 1978}) \quad (2.29)$$

the superscript denotes that the Green function is calculated on a graph in which the superscripted vertices are absent and

$$Q_{ren}^{(n)}(z) = \sum_{n=0}^{\infty} \sum_{\beta_n \in d_n^i} K'(C_{\beta_n}^{(n)}) \quad (2.31)$$

where  $d_n^i$  are the set of non-intersecting path of length  $n$  from  $V_1$  to  $V_1$  on the lattice. The expression is identical to Feynberg renormalized perturbation expansion.

On the Augmented Space each vertex is specified by two indices : one referring to the site on the lattice and the other the configuration.

Configurations may be conveniently labelled as follows:

$$|E_0\rangle = n^0 |E_0^{(1)}\rangle$$

$$|E_{j,j+1}\rangle = n_{j,j+1}^0 |E_0^{(1)}\rangle \quad n_{j,j+1}^1 |E_0^{(2)}\rangle$$

## 2.32 THE CPA IN THE GRAPHICAL METHOD

The CPA retains superpositions of all paths between vertices having the same configuration and different sites or the same site and configuration that differ only at that site e.g.  $|s, f_\mu\rangle$  and  $|s, f_{\mu'}\rangle$ .

The *Augmented space*  $(\mathcal{H} \oplus \mathcal{H})$  (Hamiltonian in the site-configuration representation  $|\alpha f\rangle$ ) is given by

$$\tilde{H}_{\alpha f, \alpha' f'} = H_{\alpha f, \alpha' f'}^c + V_{\alpha f, \alpha' f'} \quad (2.32)$$

where,  $H_{\alpha f, \alpha' f'}^c$  is an operator in the configuration space associated with the probability distribution and  $V_{\alpha f, \alpha' f'}$  is an operator in  $\mathcal{H}$ . The states in the configuration space are specified by the set  $\{|f_i^c\rangle\}$ . In general, we choose a basis such that the representation of  $H^c$  is tri-diagonal so that  $p(x)$  is expressed as a continued fraction. For a bimodal density the  $H_{\alpha f, \alpha' f'}^c$  for each  $\alpha$  is given by equation (2.15) and the graph is a single link chain like (Fig 2.3a). Finally the configuration averaged Green function is the resolvent corresponding to the Hamiltonian  $\tilde{H}$ .

The configurationally averaged Green function  $\langle G_{\alpha\alpha'}(z) \rangle$  can be determined by considering self avoiding paths between  $|\alpha f_0\rangle$  and  $|\alpha f_n\rangle$  in the complete *Augmented space*  $\mathcal{H} \oplus \mathcal{H}$ . In





Fig. 2.2a Representation of a single link chain

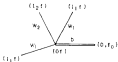


Fig.2.2b CFA graph in augmented space

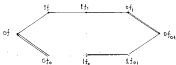


Fig. 2.2c Shortest self-avoiding, closed loop in the full augmented space involving both spatial and field hops.

$\Phi$ , an electron at site labelled by  $n$  and configuration state  $|x_{1n}, x_n\rangle = |x_1^n\rangle \otimes |x_2^n\rangle \dots |x_N^n\rangle$  can either make spatial hops to one of the near neighbours of  $n$  with matrix element  $T$ , keeping the configuration state the same, or it can remain on the spatial site, while the configuration only at that site changes while those at all other sites remain the same. This too is with matrix element  $H$ .

$$\langle \Phi_{lm}(s) | = \langle n | x_n | (iE - \hat{H})^{-1} | x_n \rangle \quad (2.22)$$

Here, the problem is reduced to that of an ordered system with a much simplified set of eigen functions.

Now starting from the vertex (0) the first steps in the self-avoiding paths possible are the near neighbours  $1_n$  in the real space shown by the single lines in figure (2.2b) or to different configuration states of the site 0 (For example the one labelled by  $\Phi_{1n}$ ) shown by double lines in the same figure.

If  $P_0(z)$  is the contribution of all self avoiding paths from vertex 0 and back in the Hilbert space  $\mathcal{H}$ , then the resolvent is an ordered system in

$$P_{\text{res}}(z) = \frac{1}{z - R_0(z)} \quad (2.34)$$

In the three dimensional case  $R_0(z)$  will include the contribution  $\sum_i V_i^{\text{sp}} P_{\text{res}}^{(i)}$  (where  $i$  are the various neighbours of 0 and  $P_{\text{res}}^{(i)}$  is the resolvent calculated from a sub graph in which the vertex 0 is removed), as well as the contributions of closed self avoiding loops in  $\mathcal{W}$ . In the extended space, the configuration averaged Green function is given by

$$\langle G(z) \rangle = \frac{1}{z - R(z) - T(z)} \quad (2.35)$$

$R(z)$  is the contribution of non intersecting paths from the vertex 0f and back that are either (a) entirely in the spatial part of the Augmented space which is same as those that contribute to  $R(z)$ , or (b) self avoiding paths in the Augmented space which includes field-hops but do not form closed loops.  $T(z)$  is the contribution of the closed non intersecting loops from 0f in the full Augmented space.

Figure (2.3c) shows a self avoiding closed loop involving both spatial and field hops. There are numerous loops like this and it is almost impossible to account for all of them. So as an approximation we assume that all closed

paths having both spatial and field hops be delimited i.e.  $T(a) \neq 0$ . Once we have done that, our approximate graph will have the following topology : (a) from every spatial site there is now an extra field hop with link function  $M$ . Every vertex looks like figure (E.3b); and (b) if starting from a vertex ' $af_0$ ' we hop to a vertex ' $af_1$ ' then the subgraph with vertex ' $af$ ' missing is an infinite graph exactly similar to the original one. A direct consequence of this property is

$$G_{af_0, af_0}^{\text{del}} = G_{af_0, af_0} = \langle G_{af_0} \rangle \quad (E.3c)$$

This will not hold in the absence of delinking as above.

Let  $G^{\text{del}}(z)$  be the resolvent, corresponding to the delimited graph in the Augmented space and let

$$M_{ij} = \delta_{ij} \delta_{i-1}$$

be the tridiagonal representation of the operator  $M^0$  in the each subspace  $|f_a^{(i)}\rangle$  of  $|f_a\rangle$ . Then

$$\begin{aligned} G^{\text{del}}(z) &= \frac{1}{[z - G_0(z - M^0 G_1(z)) - M^0 G_1(z)]} \\ &= P_{\text{del}}^{-1} = -G_1^{-1} G_1(z) \end{aligned} \quad (E.3d)$$

$$\text{where, } G_0(z) = \frac{1}{z - E_0(1 - U_0^2 G_0) - U_{1,0}^2 U_{1,0} G_1(z)} \quad (2.36)$$

In the conventional CPA formalism, the self energy  $\Sigma(z)$  is expressed as

$$\begin{aligned} G^{\text{CPA}}(z) &= \frac{1}{z - \Sigma(z) - U_0(z-E)} \\ &= E_0 [z - E(z)] \end{aligned} \quad (2.37)$$

Equations(2.36) and (2.37) show the equivalence. Equivalence of the two has been discussed in detail by Bishop and Rockwood (1974).

## 2.6 THE CLUSTER GENERALIZATION : THE SELF-CONSISTENT EXACTING METHOD IN ADAPTED SPACE

The generalization to a CPA with a cluster given by the sites  $\{x, y, \dots, v\}$  retains contribution of all paths between vertices having the same configuration and different sites or between the same site  $x$ , and configurations which differ only at those sites which belong to the same cluster as  $x$ , e.g.  $|x, \bar{x}_y\rangle$ ,  $|x, \bar{x}_{xy}\rangle$ ,  $|x, \bar{x}_{xyx}\rangle, \dots, |x, \bar{x}_{xyv}\rangle$

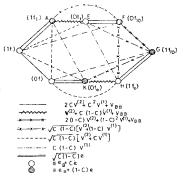


Fig. 2.4a Octagonal decomposition corresponding to 2DFA in augmented space.

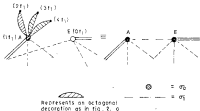


Fig. 2.4b Renormalization of site and bond of the octagon in ASF due to infinite medium.

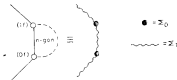


Fig. 2.4a Final renormalized site and bond in ASF for the octagon in Fig. 2.4a

The polygonal self avoiding paths which take into account the multiple scattering within the cluster are immersed in the rest of the lattice and consequently the vertices and links (bonds) have to be renormalized accordingly. We will as an example see how this is done for the SCF's for a binary alloy. Corresponding to the 2-site cluster, we have an octagonal decoration of self avoiding polygonal paths as the Augmented Space graph shows in the figure (2.4a). The eight vertices of the octagon correspond to the eight different configurations of the two site cluster ( $2 \times 2^2$ ). The octagon belonging to a bond has no connection to another bond through links in the Augmented Space, which effectively ensures that the correlated scattering from three or more sites belonging to different bond is ignored.

Finally, we renormalize the vertices and bonds in the following way. The renormalization is a two step process.

#### STEP 1

The decorating octagon is set as isolated octagon involving only the two spatial sites( $i$  and  $j$ ). If we consider the vertex  $A$  ( $i\downarrow$  in the notation of Masekjee(1973)) the bond  $AB$  ( $i\downarrow$  to  $B\downarrow$ ) belonging to the octagon is only one of the 2 nearest neighbours of  $i$ . The other remaining (3-1) bonds viz  $i\downarrow$  to  $B\uparrow, B\downarrow, \dots$  etc. also hang on to site  $A$ . Besides, these bonds themselves in turn have their octagons



decorating them (Fig 2.4b). Thus the bond AE is itself immersed in a self-consistent medium. The same is true for the bonds FG and HK of the octagon. We may take this into account by saying that the medium renormalizes the bonds AE, FG and HK and the sites at their extremities. Once this renormalization is carried out, the octagon is effectively isolated. The renormalized vertices  $\pi_a(z)$  and bonds  $\pi_b(m)$  are found as below:

We divide the whole lattice into two subspaces labelled by (1) and (2). (1) is a unrenormalized bond AE with a Hamiltonian

$$H^{(1)} = \sum_a (T_{AE} + T_{EA}) \quad (2.40)$$

and (2) a lattice  $E$  which is the original lattice minus the link AE and in which all bonds and sites are renormalized.

This has a Hamiltonian

$$H^{(2)} = \sum_a \sum_{b \neq a, E} P_{ab} + \sum_{b \neq a, E} T_{ab} \quad (2.41)$$

also there is a linking Hamiltonian between (1) and (2).

$$H^{(12)} = \sum_a \sum_b (T_{ab} + T_{ba} + T_{ba} + T_{ab}) \quad (2.42)$$

Now Green's operator corresponding to the subspace (1),

$$G^{(2)} = P_1 \otimes P_1 = \{ \alpha I - H^{(2)} - \alpha^{(2)11} \alpha^{(2)22} H^{(2)11} \}^{-1} I \quad (2.43)$$

where,  $\alpha^{-1}$  is the inverse of the operator  $\alpha$  in the subspace  $Y$ .

$G$  is Green's operator in the total space and  $G^{(2)}$  is  $(\alpha I - H^{(2)})^{-1} P_1$  with

$$P_1 + P_2 = I \quad (2.44)$$

It is obvious from above equation that the effect of the rest of the lattice hanging on to the bond  $AB$  is to change the Hamiltonian  $H^{(2)}$  to  $H^{(2)} + \alpha$  where the self energy  $\alpha$  is given by

$$\begin{aligned} \alpha_{AA} = \alpha_{BB} = \alpha_1(z) &= t_1^2(z) \sum_{k, \text{nn } A} G_{kA}^{(2)} \\ \alpha_{AB} = \alpha_{BA} = \alpha_2(z) &= t_1^2(z) \sum_{k, \text{nn } A} \sum_{k', \text{nn } B} G_{kA}^{(2)} G_{k'B}^{(2)} \end{aligned} \quad (2.45)$$

where,  $N_A$  are the nearest neighbour of  $A$  ;  $N_B$  are the nearest neighbour of  $B$ .

## STEP 2

We are now left with the isolated unsolved

octagon. This octagon is to be renormalized again because each of the vertices such as  $\bar{A}, E$  etc are connected with other vertices through either a field hop or spatial hop. For carrying out this final renormalization we divide the octagon into two suboctagons : bond  $\bar{B}$  ( $\bar{D}, I, F$ ) and the rest of the octagon  $\bar{H}$ .

$$\bar{H}^B = \sum_{i,j} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} \bar{H}_{ij}^{\alpha\beta\gamma\delta\epsilon\zeta} ; \quad \bar{H}^H = \sum_{i,j} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} \bar{H}_{ij}^{\alpha\beta\gamma\delta\epsilon\zeta} \quad (2.46)$$

$$\bar{H}^{BH} = \sum_{i,j} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} ( \bar{H}_{ij}^{\alpha\beta\gamma\delta\epsilon\zeta} + \bar{H}_{ji}^{\alpha\beta\gamma\delta\epsilon\zeta} ) \quad (2.47)$$

Now, we have as before,

$$\begin{aligned} d^B &= P_B \otimes P_B \\ &= [ d^B - \bar{H}^B - \bar{H}^{BH} d^H \bar{H}^{BH} ]^{-1} P_B \end{aligned} \quad (2.48a)$$

$$\text{and } d^H = [ d^H - \bar{H}^H ]^{-1} P_H \quad (2.48b)$$

Now we have the final renormalized site  $\bar{X}_S(2)$  and bond  $\bar{P}_S(2)$  given by :

$$\bar{X}_S(2) = \bar{H}_{ss}^B + \sum_{j \neq s} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} \bar{H}_{sj}^{\alpha\beta\gamma\delta\epsilon\zeta} d_{jk}^H \bar{H}_{ks}^{BH} \quad (2.49)$$

$$\bar{P}_S(2) = \bar{H}_{ss}^H + \sum_{j \neq s} \sum_{\alpha\beta\gamma\delta\epsilon\zeta} \bar{H}_{sj}^{\alpha\beta\gamma\delta\epsilon\zeta} d_{jk}^H \bar{H}_{ks}^{BH}$$

Equations (2.45) and (2.49) are the set of self consistent form of Equations which provides self consistent effective medium.

$$\mathbf{Z} = \begin{bmatrix} \mathbf{Z}_0 & \mathbf{Z}_1 \\ \mathbf{Z}_1 & \mathbf{Z}_0 \end{bmatrix} \quad (2.50)$$

The Green function may now be calculated

$$\begin{aligned} \mathbf{H}_{\text{eff}} &= \sum_i \mathbf{Z}_0 \mathbf{F}_i + \sum_i \mathbf{Z}_1 \mathbf{F}_{i+1} \\ &= \mathbf{Z}_0 \mathbf{I} + (\mathbf{Z}_0/\nabla) \mathbf{Z} \nabla \mathbf{F}_1 \\ &= \mathbf{Z}_0 \mathbf{I} + (\mathbf{Z}_0/\nabla) \mathbf{h}_0 \end{aligned} \quad (2.51)$$

where  $\mathbf{h}_0 = \mathbf{Z} \nabla \mathbf{F}_1$

$$\begin{aligned} G(\mathbf{z}) &= [\mathbf{zI} - \mathbf{H}_{\text{eff}}]^{-1} \\ &= [\mathbf{zI} - \mathbf{Z}_0/\nabla - (\mathbf{Z}_0/\nabla) \mathbf{h}_0]^{-1} \\ &= (\nabla/\mathbf{Z}_1) \mathbf{I} + (\mathbf{zI} - \mathbf{Z}_0/\nabla) \nabla (\mathbf{I} - \mathbf{h}_0)^{-1} \\ &= (\nabla/\mathbf{Z}_1) \mathcal{G}(\mathbf{z}) \end{aligned} \quad (2.52)$$

where  $\mathbf{z} = (\mathbf{z} - \mathbf{Z}_0/\nabla)/\mathbf{Z}_1$  and  $\mathcal{G}(\mathbf{z}) = (\mathbf{zI} - \mathbf{h}_0)^{-1}$

Once we calculate  $\mathcal{G}(\mathbf{z})$  by methods available for translationally symmetric Hamiltonians, the equations (2.45) to (2.52) are the basic equations governing the GCFs.

## CHAPTER III

### RECURRENCE SOLUTION TO THE SCHRÖDINGER EQUATION

#### 3.1 THE RECURRENCE METHOD

In simple metals, where the effective, screened interaction between electrons and atoms is not so strong, the electronic structure is determined by the long range periodicity of the atomic potentials. It is this aspect of physics that is exploited in the band theory to express electronic properties of the solid as a coherent superposition of the electronic properties of the atoms. However, when the electrons interact strongly with the atoms, this picture breaks down and properties no longer depend on long range periodicity, but rather on only the first few shells of neighbors of each atom. The d-electrons in transition metals are typical examples of this regime. While the band theory is still a valid formal solution to the Schrödinger equation, the physics is better understood by means of a solution that explicitly accounts for the role of the local environment.

The basic problem is to find the local density of states from a tight binding or localised orbital model. The underlying physics is the recursion method (Haydock 1990) is that the local orbital itself has the greatest effect on the local electronic structure and successively more distant orbitals have lesser effect. The solution must define a hierarchy of environments so that their relative influence is explicitly displayed in the local density of states. Physically, the local density of states is the intensity of each eigenstate on a particular atom or bond. Mathematically, it is the squared magnitude of the projection of an eigenstate on a local orbital, so that the local density of states gives the coupling of an orbital at each energy.

The problem is the determination of linear combinations of the local orbitals such that the electron must pass through each state as it diffuses away from the local orbital from which it starts. The local density of states for a basis orbital  $|\phi_a\rangle$  is determined by the sequence of environments described by orthogonal states  $|\psi_n\rangle$ , where  $|\psi_n\rangle$  is a linear combination of basis orbitals and  $|\psi_0\rangle$  is  $|\phi_a\rangle$ .  $|\psi_n\rangle$  must satisfy the condition that

$$H|\psi_n\rangle = a_n|\psi_n\rangle + b_{n+1}|\psi_{n+1}\rangle + b_n|\psi_{n-1}\rangle \quad (3.1)$$

where  $H$  is the Hamiltonian of the model and  $|\psi_n\rangle$  are

localized on the shell of atom  $n$  born from the atom accommodating  $|\varphi_n\rangle$ . The parameters  $a_n$  and  $b_n$  describe the coupling of each environment to itself and its neighbours. The purpose of going over to such a basis set is that one can transform any three dimensional model to a pseudo one-dimensional equivalent chain, which is characterized by the parameters  $a_n$  and  $b_n$  the coupling constants of each environment to itself and its neighbours.

The coefficients  $a_n$  and  $b_n$  are generated recursively from

$$\begin{aligned}
 |U_n\rangle &= |\varphi_n\rangle, \quad b_n = 1 \\
 a_n &= \frac{\langle U_n | H | U_n \rangle}{\langle U_n | U_n \rangle} \\
 b_{n+1} &= \frac{b_n \langle U_n | U_{n+1} \rangle}{\langle U_{n+1} | U_{n+1} \rangle}
 \end{aligned}
 \tag{3.21}$$

We have used the orthogonality of the new basis  $\{U_n\}$ . The above equations are a convenient algorithm for computational generation of the coefficients  $a_n$  and  $b_n$ .

As an example, the local density of states for  $|\varphi_n\rangle$  can be written in terms of the parameters of the chain model

Let us define the determinant of the matrix with the first  $n$  rows and  $n$  columns deleted as  $D_n(E)$

$$G_n(E) = \frac{D_n(E)}{D_n(E)}$$

$$= \frac{D_n(E)}{(E - \lambda_n) D_1(E) - \lambda_n^2 D_2(E)}$$

$$= \frac{i}{(E - \lambda_n) (-\lambda_n^2 D_2(E)/D_n(E))}$$

$$= \frac{i}{(E - \lambda_n) (-\lambda_n^2 G_1(E))}$$



as the continued fraction

$$g_0(E) = -(1/\alpha) \ln \{ 1/2^{1/2} (E-a_0-b_1^2/(E-a_1-b_2^2/(E-a_2-b_3^2/\dots)) \}$$

$$\text{where, } H_{nn} = a_n : H_{n,n+1} = H_{n+1,n}^* = b_n \quad (3.2)$$

Let us try to get the continued fraction for local density of states  $g_0(E)$  starting from the Green function. One can immediately check that in the above basis set  $\{|U_n\rangle$  the Hamiltonian is a tridiagonal matrix

$$\begin{bmatrix} a_0 & b_1 & 0 & 0 & \dots \\ b_1^* & a_1 & b_2 & 0 & \dots \\ 0 & 0 & -b_2^* & a_2^* & \dots \\ 0 & 0 & b_2 & -a_2 & \dots \\ \vdots & \vdots & \vdots & \vdots & \dots \end{bmatrix}$$

$$g_0(E) = \langle \Phi_0 | (zI-H)^{-1} | \Phi_0 \rangle$$

$$= \left[ \begin{array}{ccccc} (E-a_0) & -b_1 & 0 & 0 & \dots \\ -b_1^* & (E-a_1) & -b_2 & 0 & \dots \\ 0 & -b_2^* & (E-a_2) & -b_3 & \dots \\ 0 & 0 & -b_3^* & (E-a_3) & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{array} \right]^{-1}$$

Let us define the determinant of the matrix with the first  $n$  rows and  $n$  columns deleted as  $D_n(E)$

$$\begin{aligned} Q_0(E) &= \frac{D_1(E)}{D_n(E)} \\ &= \frac{D_1(E)}{(E - a_0) D_1(E) - b_1^2 D_2(E)} \\ &= \frac{1}{(E - a_0) - b_1^2 D_2(E)/D_1(E)} \\ &= \frac{1}{(E - a_0) - b_1^2 Q_1(E)} \end{aligned}$$

If we continue this process upto  $n$ -steps, we have

$$Q_0(E) = \frac{1}{E - a_0 - b_1^2 / (E - a_1 - b_2^2 / \dots (E - a_{n-1} - b_n^2 Q_n(E))} \quad (2.4)$$

where,

$$Q_n(E) = \frac{1}{E - a_n - b_{n+1}^2 Q_{n+1}(E)}$$

Thus  $Q_0(E)$  has a continued fraction representation

which in general may not terminate after a finite number of steps. It has been verified that for many systems the continued fraction converges very fast. When the convergence is slow or oscillatory it can be terminated by various termination schemes. Several termination schemes have been developed by Fox (1978,1984) and Haydock and Fox (1984).

### 3.2 CHOICE OF CONTINUED FRACTION TERMINATORS

For applying the termination scheme to approximate the tail of the continued fraction for the Green function, we have to ensure that the approximate resolvent  $R(\epsilon)$  ( which replaces  $G$  ) should be such that the corresponding Hamiltonian  $H$  should have a similar energy spectrum. If a similar energy spectrum we mean that it should possess as near singularities as the spectrum of the true Hamiltonian i.e band-edges, van Hove singularities and so on.

The continued fraction form of the Green function for a uniform chain parameter i.e  $t_n = t$  ,  $t_n = b$  is

$$G_n(E) = \frac{1}{E - \epsilon - b^2 G_n(E)}$$

$$\text{or, } b^2 G_n^2(E) - (E - \epsilon) G_n(E) + 1 = 0$$

Therefore,

$$G_p(E) = \frac{(E - \epsilon_0) \pm \sqrt{(E - \epsilon)^2 - 4B^2}}{2B^2} \quad (3.5)$$

Here we need not use the termination scheme because the Green function is exact. The negative sign is chosen in (3.5) to ensure a polelike  $G_p(E)$ . The Green function has two band edge singularities at  $E_1 = \epsilon + B$  and  $E_2 = \epsilon - B$  and a branch cut between these energies along the real energy axis.

Let us now consider a general system having a single band Hamiltonian. In this case, the square root terminator (3.4) is appropriate as shown by Haydock and New (1984). We illustrate mathematically below. We have the Green function

$$G(E) = \frac{1}{E - \epsilon_p - b_1^2 \sqrt{\dots \sqrt{E - \epsilon_{n-2} - b_{n-2}^2 \sqrt{E - \epsilon_{n-1} - b_{n-1}^2 t(E)}}} \quad (3.6)$$

where  $t(E)$  is the required terminator

Since the eigenstate of the chain is some linear combination of the states  $|U_1\rangle, |U_2\rangle, \dots$ , we write the

Schrödinger equation for the chain is the following form

$$E \sum_n^{\infty} p_n U_n = E \sum_n^{\infty} p_n U_n \quad (3.7a)$$

in matrix form:

$$\begin{bmatrix} (E-a_0) & -b_1 & 0 & \dots \\ -b_1 & (E-a_1) & -b_2 & \dots \\ 0 & -b_2 & \dots & \dots \\ \vdots & \vdots & \vdots & \dots \\ \vdots & \vdots & \vdots & \dots \\ \vdots & \vdots & \vdots & \dots \end{bmatrix} \begin{bmatrix} p_0 \\ p_1 \\ p_2 \\ \vdots \\ \vdots \\ \vdots \end{bmatrix} = 0 \quad (3.7b)$$

The recursion coefficients can be found in terms of orthogonal polynomials. We use those of the first kind  $p_1(E)$  and second kind  $q_1(E)$ . Now making a proper choice of boundary conditions such that

$$p_{-1} = 0 = q_{-1} \quad ; \quad p_0 = 1 \quad ; \quad a_0 = b_0^2 \quad (3.8a)$$

We have,

$$p_{n+1}(E) = (E-a_n) p_n(E) - b_n^2 p_{n-1}(E)$$

$$q_n(E) = (E-a_n) q_{n-1}(E) - b_n^2 q_{n-2}(E) \quad (3.8b)$$

We may write

$$Q(E) = \frac{q_{n-2}(E) + b_{n-2}^2(E) q_{n-3}(E)}{q_{n-1}(E) + b_{n-1}^2(E) q_{n-2}(E)} \quad (3.9)$$

### 3.2 TERMINATOR SCHEMES

We have three termination techniques, of which two are explicit and require further physical input in the form of analytic properties of the Green function, while in the third case no further assumptions are required and is implicit in terms of the terminator function  $t(E)$  in equation (3.8). Haydock (1983) and Haydock and Yau (1984) have provided two explicit termination techniques based on generating an analytic form for  $q(E)$  for the single band density of states and for many band case respectively. The third method is an implementation of the quadrature approach.

For the case of single band density of states, the square root terminator is appropriate and we have

$$u(E) = \frac{\{ E - (a+b)/2 - \sqrt{(E-a)(E-b)} \}}{2\pi^2} \quad (3.10)$$

where  $E = a$  and  $E = b$  correspond to the band edges and  $b = (b-a)/4$ . In the miniband case, we use a model Greenian F(E) [Haydock and New(1984)], with square root band-edge singularities,

$$F(E) = \sum_j H_j [E - (a_j + b_j)/2 - \sqrt{(E-a_j)(E-b_j)}] / s_j^2 \quad (3.11)$$

Here  $a_j$ 's,  $b_j$ 's and  $H_j$ 's are respectively the left band edges, the band widths and the band weights (the number of states in the  $j^{th}$  band) as  $j$  runs over all the bands. The continued fraction corresponding to  $F(E)$  is generated using the recursion algorithm with  $H$  replaced by  $E$ , vectors by polynomials and the vector inner product by that generated by  $F$ . Based on classical generation of orthogonal polynomials [Cheney, 1955], Haydock and New (1984) described the inner product for this particular Greenian as a union of Gauss-Chebyshev quadratures:

$$\langle f, g \rangle = \sum_{j=1}^n \sum_i w_{ij} f(x_{ij}) g(x_{ij}) \quad (3.12)$$

where,  $\alpha_{n+1} = \pi R / (n+1) \sin^2 \theta$  ;  $\alpha_n = \alpha_{n+1}(1 - \cos \theta)$ ,  $\theta/2$

and  $\theta = \pi / (n+1)$

This provides the general form of terminator for most three-dimensional model calculations. In case other analytic forms  $F(E)$  are required one can use the supplied basic routines to generate the corresponding three term recurrence explicitly or through the use of an appropriate numerical quadrature rule. Let  $v_1(E)$  and  $u_1(E)$  be the orthonormal polynomials corresponding to  $F(E)$  just as we have  $p_1$  and  $q_1$  for  $G(E)$  before, then the terminator is given by

$$v(E) = \frac{u_{n+2}(E) - F(E) v_{n+2}(E)}{d_{n+2}^2 [u_{n+2}(E) - F(E) u_{n+2}(E)]} \quad (3.13)$$

The third termination scheme, the quadrature approach does not generate  $v(E)$  explicitly, but in some sense averages over all possible values of  $v(E)$ . In this case, the integral density of states

$$N(E) = \int_a^E n(x) dx \quad \text{is approximated by} \quad \sum_{K_i \in E} w(K_i) \rightarrow w(E) \quad (3.14)$$

where  $\alpha$  is a constant which usually takes the values 0.5 and  $K_i$ 's are the Eigen values of the Jacobi matrix (3.2)



extended by generating a new coefficient.

$$a_{n+1} = E - b_{n+1}^2 E_{n+1}(E) / E_{n+1}(E) \quad (3.15)$$

This ensures that at least one of the  $E_k$  or  $E_n$  is equal to  $E$ .

Then the density of states is approximated by

$$a(E) = \frac{E_2'(E)}{E_{n+1}(E)} \left[ \sum_{i=1}^{n-1} \frac{\partial \omega_i}{\partial E_{n+1}} + \frac{\partial \omega_n}{\partial E_{n+1}} \right] \quad (3.16a)$$

$$\omega_i = \omega(E_i) = a_{n+1}(E_i(E)) / E_2'(E_i(E)) \quad (3.16b)$$

$$\frac{\partial \omega_i}{\partial E_{n+1}} = [4(E_{n+1} E_{n+1} - E_i (E_{n+1}^2 E_{n+1}' - E_i^2 E_{n+1}'))] / (E_{n+1}')^2_{E=E_i} \quad (3.16c)$$

If  $\alpha$  is a function of  $E$ , the above expressions are then modified and the library routines can be used as they stand as the output contains all information needed in the generalisation.

Sometimes it is useful to evaluate  $\omega(E)$  without explicit calculation of  $E_i$ , then the Christoffel-Barrow theorem [Chilars ,1958] enables us to write a more independent form:

$$v(E) = \frac{P_{n+2}(E)q_{n-1}(E) - P_{n-1}(E)q_{n+2}(E)}{P_{n+2}(E)P_{n-1}^*(E) - P_{n-1}^*(E)q_{n+2}(E) + P_{n+2}^*(E)P_{n-1}(E)} \quad (3.17)$$

### 3.3 APPLICATION TO d-STATES:

Let us consider the one electron treatment of the d-bands of an fcc metal, say Nickel. The states of the atom are the five atomic-like orbitals with d-symmetry on each atom. They are taken to be orthogonal to other orbitals on other sites. The Hamiltonian describes hopping of an electron from atom to atom induced by overlap of orbitals on one site with the potential of a nearest neighbor site. This hopping is described by the three Slater-Koster parameters  $dd\sigma$ ,  $dd\pi$  and  $dd\delta$ . The elements of  $H$ , that is, hopping parameters between orbitals on nearest neighbor atoms, are determined by performing the appropriate rotation, obtaining values that in general depend on  $dd\sigma, dd\pi, dd\delta$ . We approximate the crystal by a cluster of four unit cells of fcc lattice, containing 32 atoms.

In order to model the behavior of a d-electron in an infinite crystal, we choose initial states in the center of the cluster as having an environment most like the crystal. In an infinite fcc crystal, d-orbitals can be chosen

TABLE 3.1

Chain Substitutions of  $\mathbb{Z}_2$  in  $\mathbb{Z}_2$  and  $\mathbb{Z}_4$  in  $\mathbb{Z}_4$ 

$\alpha$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$
Subcase I				
0	0 0	0 0 0 0 0 0 0 0	0 0	0 0 0 0 0 0 0 0
1	-0 1 0 0 0 0 - 00	0 1 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 1 0 0 0 0 - 00
2	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
3	-0 0 0 0 0 0 - 00	0 1 1 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
4	-0 1 0 0 0 0 - 00	0 1 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
5	-0 0 0 0 0 0 - 00	0 1 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
6	-0 0 0 0 0 0 - 00	0 1 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
7	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
8	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
9	-0 0 0 0 0 0 - 00	0 1 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
10	0 0	0 0 0 0 0 0 0 - 00	0 0	0 0 0 0 0 0 - 00
Subcase II				
0	0 0	0 0 0 0 0 0 0 - 00	0 0	0 0 0 0 0 0 - 00
1	-0 1 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
2	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
3	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
4	-0 1 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
5	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
6	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
7	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
8	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
9	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
10	0 0	0 0 0 0 0 0 0 - 00	0 0	0 0 0 0 0 0 - 00
Subcase I				
0	0 0	0 0 0 0 0 0 0 - 00	0 0	0 0 0 0 0 0 - 00
1	-0 1 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
2	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
3	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
4	-0 1 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
5	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
6	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
7	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
8	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
9	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 0 - 00	-0 0 0 0 0 0 - 00	0 0 0 0 0 0 - 00
10	0 0	0 0 0 0 0 0 0 - 00	0 0	0 0 0 0 0 0 - 00

so that there are only two that are non-equivalent : one coupling to the  $E_g$  states and the other coupling to the  $T_{2g}$  states. The cluster selected does not possess the full point group symmetry of the fcc lattice. The  $T_{2g}$  symmetry is split by the cluster boundary into a doublet and a singlet while the  $E_g$  doublet is also split.

Table 3.1 lists parameters for the first 11 levels for chains initiated by each of the five orbitals on the central atom of the cluster. There are a total of 315 degrees of freedom which is quite modest for a calculation of this type but serves for illustration. The chains have not terminated but considerable information can be derived from them. The first few levels of the chains display the triply degenerate  $T_{2g}$  and the doubly degenerate  $E_g$  symmetries. This is because until the chain states involve atoms on the boundary of the cluster, they have the full point group symmetry of the lattice. At the third level, the boundary splits the two lattice symmetries and this enables us to see the effect of the boundary. There is little to learn from the chain states except that because the Hamiltonian involves only nearest neighbour hopping, the weight of the states moves outward with each level until the states hit the boundary and reflect off it. The behaviour of the states is analogous to the free electron example, although the medium is discrete rather than continuous.



Fig. 3.1 The fcc d band local density of states as derived from a recursion method calculation on a cluster of 2 1000 atoms using (a) 5- and (b) 30 levels, respectively of the continued fraction expansion.

### 3.31 THE d BAND DENSITY OF STATES OF NICKEL

Figures 3.1 (a) and (b) show the d band density of states of pure Nickel as derived from a recursion method calculation on a cluster of  $\sim 1000$  atoms using 8 and 20 levels respectively, of the continued fraction expansion. The centre of the band is near the zero of the energy scale for the up band of Nickel. The band starts from about -0.1 Ryd and continues upto 0.1 Ryd. The down band is however shifted slightly to the right (about 0.02 Ryd ). The starting values of the band centres were taken from Hasegawa and Kanamori (1972). The scale used in their calculation was however different from the one used in the Recursion method. We therefore utilized a conversion scale:  $E^{HKK} = 0.14 E^{RM} + 0.077$  for converting different energy values from Hasegawa scale to the Recursion scale. The Fermi level for Nickel in the Recursion was at 0.077 whereas in the Hasegawa it was at zero. The band centres were later self consistently calculated.

## CHAPTER IV

### ELECTRON CORRELATION IN NARROW ENERGY BANDS

#### 4.1 INTRODUCTION

Transition and rare earth metals have in addition to their conduction bands, partly filled d or f-bands, which give rise to the characteristic properties of these metals. Correlation phenomena are of great importance in determining the properties of these narrow energy bands, indeed more important than the corresponding effects in conduction bands. Since these d or f-electrons are relatively more localized i.e. the band widths are narrower than the conduction bands, the free electron gas does not provide a good model for these bands. Therefore, a theory of correlation which adequately takes into account the atomic nature of the solid is required. In the case of f-electrons of rare-earth metals, for most purposes a purely atomic (also referred to as Hottel-London or Localized) model will suffice. The same is not true for the d-electrons of the transition metals. Similarly correlation effects in a fully free electron gas

also is rather different in nature from the correlation effects in narrow energy bands.

The electron charge density in  $d$ -band is dense near the ion cores of the solid and sparse between them. That is why it is possible to assign an electron to a particular atom. This situation gives rise to the possibility of an localized description of the  $d$ -band despite its band-width.

Experimentally, it has been observed that the  $d$ -electrons of the transition metals exhibit characteristics of both ordinary band model and the atomic model. Therefore, a theory of correlation in  $d$ -bands (in transition metals) should try to strike a balance between band like and atomic like behaviour.

In its simplistic form, the atomic theory pictures a transition metal as a collection of (say singly charged) ions immersed in the conduction electron gas and interacting with each other in much the same way as the corresponding ions in salts. If the effective number of  $d$ -electrons is non-integral, this simple picture breaks down. However, it is possible to substitute for it a less restrictive model which nevertheless guarantees most of the characteristic properties of the atomic model. It is sufficient to assert that, despite the band nature of  $d$ -electrons, the electrons on any atom are strongly correlated with each other but only



weakly with electrons on other atoms. Such intra-atomic correlations are inevitable and the metal behaves to some extent according to the predictions of the atomic model.

The situation can be made clear by considering an example. Let us first consider a partly filled d-band of non-interacting electrons. In such a system the spin of an atom (that is, the total spin of all the electrons on that atom) is a quantity which fluctuates randomly in magnitude and direction. The characteristic time of fluctuation is of the order of the d-electron hopping time that is, the time in which a d-electron hops from one atom to another in the course of its band motion:  $\tau \approx \hbar/\Delta$  where  $\Delta$  is the d electron band width. In this situation, one can think of spins being associated with each of the moving d-electrons.

We now switch on the electronic interactions. Hund's first rule for atoms which says that the intra-atomic interactions align the electron spins on an atom, will be useful since a similar effect in a metal is expected. Let us suppose now that the electrons have their spins quantized in what will be called the up and down directions and that at some instant a given atom has its total spin in the up direction. Then, by Hund's rule, the intra-atomic interactions are of such a nature that this atom tends to attract electrons with up spin and repel those with down spin. In

this way the property of an atom having a given total spin at some instant tends to be self-perpetuating. If these intra-atomic forces are strong enough to produce appreciable correlations, then it follows that the state of total spin up or an atom may persist for a period long as compared to the d-electron hopping time. This persistence of the atomic spin state is not due to the same up spin electron being localised on the atom. The actual electrons on the atom are always changing as a result of their band motion, but the electron motions are correlated in such a way as to keep a preponderance of up spin electrons on the atom. In these circumstances (i.e. when the correlations are strong enough) one can think of the the spin as being associated with the atom rather than with the electrons and the possibility of an atomic or Heisenberg model emerges.

The above example illustrates the possibilities of the situation. Thus one may still assume the electrons to move rapidly from atom to atom as assumed in the band model, their motion may be correlated in such a manner as to give properties characteristic of the atomic theory. That is how the electrons can exhibit both types of behaviour simultaneously. The degree of atomic behaviour exhibited depends upon the strength of the correlations.

Thus an important requirement of a theory of correlation in narrow energy bands is that it has the

property of reducing to the atomic solution in the appropriate limit i.e. when applied to a hypothetical system of atoms on a lattice but widely separated from each other and interacting only weakly. Hubbard (1963) in his famous paper describes a very simple approximate theory fulfilling the above requirement. We describe his formulation below.

## 4.2 MATHEMATICAL FORMULATION

Let us consider a hypothetical partly filled narrow d-band containing  $n$  electrons per atom. The Bloch functions of the band will be denoted by  $\psi_k$  and the corresponding energy by  $E_k$  where  $k$  is the wave-vector. These wave functions and energies are assumed to have been calculated in some appropriate Hartree-Fock potential representing the average interaction of the d-band electrons with the electrons of the other bands besides the  $n$  electrons per atom of the d-band itself. The Hartree-Fock potential is assumed to be spin independent, as a result we have the same energies and wave functions for both spins.

We take  $C_{k\sigma}$  and  $C_{k\sigma}^\dagger$  to be the usual destruction and creation operators respectively for electrons in the Bloch state  $(k, \sigma)$  where  $\sigma = \pm 1$  is the spin label. The dynamics of electrons of the band is represented approximately by the Hamiltonian

$$\begin{aligned}
H = & \sum_{\mathbf{k}, \sigma} E_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \sum_{\sigma_1, \sigma_2} \langle \mathbf{k}_1, \mathbf{k}_2 | 1/r | \mathbf{k}_1', \mathbf{k}_2' \rangle \\
& \times c_{\mathbf{k}_1', \sigma_1}^{\dagger} c_{\mathbf{k}_2', \sigma_2}^{\dagger} c_{\mathbf{k}_2, \sigma_2} c_{\mathbf{k}_1, \sigma_1} \\
& - \sum_{\mathbf{k}, \sigma} \sum_{\sigma'} \left\{ \sum_{\mathbf{k}'} \langle \mathbf{k} \mathbf{k}' | 1/r | \mathbf{k}' \sigma \rangle \right\} n_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma'}
\end{aligned} \quad (4.1)$$

where  $\mathbf{k}$  runs over the first Brillouin zone and

$$\langle \mathbf{k}_1, \mathbf{k}_2 | 1/r | \mathbf{k}_1', \mathbf{k}_2' \rangle = \int \frac{u_{\mathbf{k}_1}^*(\mathbf{r}) u_{\mathbf{k}_1'}(\mathbf{r}) u_{\mathbf{k}_2}^*(\mathbf{r}) u_{\mathbf{k}_2'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad (4.2)$$

The first term in (4.1) represents the band energy of the electrons and the second their interaction energy. The last term subtracts the potential energy of the electrons in that part of the Hartree-Fock field arising from the electrons of the band itself. The third term in equation (4.1) is there in order to avoid counting the interactions of the electrons of the band twice: once explicitly in the Hamiltonian and then implicitly through the Hartree-Fock field determining  $E_{\mathbf{k}}$ . The  $n_{\mathbf{k}}$  are the summed occupation

numbers of the states of the band in the Hartree Fock calculation, assuming up and down spin states to be occupied equally.

It is now convenient to go over to a tight binding representation of the Hamiltonian by taking recourse to the Wannier functions

$$\psi(\vec{r}) = N^{-1/2} \sum \psi_N(\vec{r}) \quad (4.3)$$

where  $N$  is the number of atoms. One can write

$$\phi_{\vec{k}}(\vec{r}) = N^{-1/2} \sum e^{i\vec{k} \cdot \vec{R}_l} \phi_l(\vec{r}-\vec{R}_l) \quad (4.4)$$

where the sum runs over all the atomic positions  $\vec{R}_l$ . Introducing the creation and destruction operators  $c_{l\sigma}^\dagger$  and  $c_{l\sigma}$  for an electron of spin  $\sigma$  in the orbital state  $\phi_l(\vec{r}-\vec{R}_l)$ . One can write

$$c_{\vec{k}\sigma} = N^{-1/2} \sum_l e^{i\vec{k} \cdot \vec{R}_l} c_{l\sigma} \quad ; \quad c_{\vec{k}\sigma}^\dagger = N^{-1/2} \sum_l e^{-i\vec{k} \cdot \vec{R}_l} c_{l\sigma}^\dagger \quad (4.5)$$

Then the Hamiltonian (4.1) can be rewritten as

$$H = \sum_{i,j} T_{ij} c_{20}^{\dagger} c_{20} + \frac{1}{2} \sum_{i,j} \sum_{\sigma,\sigma'} \langle ij | 1/r | ik \rangle c_{20}^{\dagger} c_{20}^{\dagger} c_{2\sigma} c_{2\sigma'} + c_{10} c_{10} \\ + \sum_{i,k} \sum_{\sigma} \langle ik | 1/r | 00 \rangle v_{i0} c_{1\sigma}^{\dagger} c_{1\sigma} \quad (4.6)$$

$$\text{where, } T_{ij} = N^{-3} \sum_{\mathbf{k}} E_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \quad (4.7)$$

$$\langle ij | 1/r | ik \rangle = e^2 \int \frac{d^3(\mathbf{r}-\mathbf{R}_i) d^3(\mathbf{r}-\mathbf{R}_k) d^3(\mathbf{r}-\mathbf{R}_j) + (\mathbf{r}-\mathbf{R}_k) + (\mathbf{r}-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{R}_i|} \\ \times d^3\mathbf{r} d^3\mathbf{r}' \quad (4.8)$$

$$\text{and } v_{i0} = N^{-3} \sum_{\mathbf{k}} v_{\mathbf{k}} e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_0)} \quad (4.9)$$

We will now make the essential simplifying approximation. Since we are dealing with narrow energy bands the Wannier function  $\phi$  will closely resemble atomic functions. Also, if the band width is small, these  $\delta$ -functions must form an atomic shell which has a radius small compared to the inter atomic spacing. From equation (4.6) it may be seen that in this circumstance the integral  $\langle ij | 1/r | ik \rangle = U$  will be much greater in magnitude than any of the other integrals (4.8), suggesting that all the integrals (4.8) maybe neglected in comparison to  $U$ . Making this approximation the Hamiltonian of (4.6) reduces to

$$H = \sum_{l,j} T_{lj} c_{lj}^{\dagger} c_{lj} + \frac{1}{2} U \sum_{lj} n_{lj} n_{l-j} \\ - U \sum_{lj} v_{lj} n_{lj} \quad (4.10)$$

where  $n_{lj} = c_{lj}^{\dagger} c_{lj}$ . From (4.8)  $v_{lj} = \frac{1}{2} \frac{1}{r_{lj}} = 1/2$

So, the last term of equation (4.10) reduces to

$$- \frac{1}{2} U n \sum_{lj} n_{lj} = - \frac{1}{2} U n^2 = \text{const.}$$

and may, therefore, be dropped after a redefinition of the zero of our energy scale. Equation (4.10) is the approximate Hamiltonian used hereafter.

Many approximations have been made in the derivation of the simplified Hamiltonian (4.10). We will now examine the validity of these approximations as applied to the case of 3d-electrons in the transition metals.

The most obvious approximation has been the neglect of all the interaction terms in equation (4.8) other than U. For the sake of comparison, one has to note that U has the order of magnitude  $\sim 10$  eV for 3d electrons in transition metals. The largest of the neglected terms are those of the type  $(1j|1/r|1j)$  where  $i$  and  $j$  are nearest neighbours. From

(4.8) these integrals can be estimated to have the order of magnitude  $(1/R|R_{ij}| \approx 5 \text{ eV}$  ( $R$  = inter atomic spacing in Bohr units). This figure, however, gets reduced appreciably when we allow for the screening of the interactions of electrons on different atoms by the conduction electron gas. This screening effect is taken into account by multiplying the above estimate by a factor of  $e^{-\lambda R}$  where  $\lambda$  is an appropriate screening constant. In the case of 3d-transition metals  $e^{-\lambda R} \approx \frac{1}{2} - \frac{1}{3}$ , reducing the  $\langle ij|1/r|ij\rangle$  term to the order of magnitude 2 to 3 eV. For the case in which  $i$  and  $j$  are not nearest neighbours

$$\langle ij|1/r|ij\rangle \approx \frac{2\pi^{-2}|\vec{R}_i - \vec{R}_j|}{|\vec{R}_i - \vec{R}_j|} R_{ij}$$

which falls off rapidly with increasing  $|\vec{R}_i - \vec{R}_j|$ , on account of the exponential factor. Thus the term

$$\frac{1}{2} \sum_{ij} \sum_{mn} \langle ij|1/r|ij\rangle a_{ip} a_{jq} \quad (4.11)$$

in equation (4.6) can perhaps be neglected as compared to  $\bar{U}$  as a first approximation.

The other neglected terms are of the type

$$\langle ij|1/r|ij\rangle \approx 4 \text{ Ryd} \approx 0.5 \text{ eV}$$



$$\langle 13 | 1/r | 1k \rangle \approx \frac{1}{4} q R_{yd} \approx 0.1 \text{ eV}$$

$$\langle 11 | 1/r | 12 \rangle \approx \langle 21 | 1/r | 12 \rangle \approx q^2 R_{yd} \approx 0.025 \text{ eV}$$

where 1, j and k are all nearest neighbours, and  $q = 0.08$  is the overlap charge (in units of  $e$ ) between two  $3d$ -electrons on nearest neighbour atoms. All other interaction terms in equation (4.8) which have been neglected are still smaller than those which one sees are already small compared to those of equation (4.11)

Another approximation that has been made use of is that only the interactions among  $3d$ -electrons is considered, the interaction with electrons of the other bands being represented only through the Hartree-Fock field. In estimating the order of magnitude of the terms of equation (4.11) due allowance was made for the screening effects of the conduction electron gas on the interactions. So, the question arises as to whether there is a similar screening effect reducing the energy of  $U$ . There is, in fact, such an effect. The speed with which  $d$ -electrons move from atom to atom is slow compared to the velocity of a typical conduction electron and, therefore, the latter can correlate efficiently with the  $d$ -electrons and screen their fields. Thus, if a given atom has an extra  $d$ -electron, its negative charge will repel conduction electrons producing a correlation hole about atom in the conduction electron sea. The presence of this

hole reduces the electrostatic potential at the atom (and, therefore, at each of its d-electrons) by about 5 eV which is the same thing as reducing  $U$  by 5 eV. This reduction though appreciable does not change the order of magnitude of  $U$ .

There is also a reduction in  $U$  by the screening of the interactions of the d-electrons by the core electrons and by the d-electrons themselves. This, however, is not a big effect because the kinetic energies of the orbital motion of the d-electrons are large compared to  $U$ . One can estimate the reduction in  $U$  due to this effect by noticing that a similar effect will occur in free atoms. In the latter case (free atoms) it has been found that these effects make the  $F^2(3d, 3d)$  and  $F^4(3d, 3d)$  parameters (using the notation of Condon and Shortley (1935) ) determined from experiment about 10 to 20 % smaller than those calculated from Hartree Fock wave functions (Watson 1968). So one may expect a reduction in  $U$  of a similar order of magnitude.

It appeared more reasonable to use in the Hamiltonian of equation (4.10) an effective  $U$  ( $\sim 10$  eV) rather than that given by the integral (4.6). The approximations involved in equation (4.10) are otherwise not so poor as to make it an unreasonable starting point for a theory of correlations for the d-band electrons. The terms omitted in going from (4.6) to (4.10) may be treated as perturbations on the solutions obtained from (4.10).

## 4.3 THE HARTREE-FOCK APPROXIMATION

One can obtain the effective Hartree-Fock Hamiltonian by linearizing the interaction terms in the true Hamiltonian. In our Hamiltonian (4.10) this is achieved by simply replacing the term  $a_{i0}^\dagger a_{i0}$  by  $\frac{1}{2} [2a_{i0}^\dagger \langle n_{i-0} \rangle + 2a_{i-0} \langle n_{i0} \rangle]$ , where  $\langle n_{i0} \rangle$  is the average of the expectation of  $n_{i0}$  over a canonical ensemble at some temperature. Dropping the last term of (4.10) (say as a constant), the Hartree-Fock Hamiltonian is reduced to

$$H = \sum_i T_{ii} c_{i0}^\dagger c_{i0} + U \sum_{i,v} a_{i0}^\dagger \langle n_{i-0} \rangle \quad (4.12)$$

Restructuring to the class of solutions for which

$$\langle n_{i0} \rangle = n_0 \text{ for all } i \quad (4.13)$$

Eqn. (4.12) reduces to

$$H_{HF} = \sum_i T_{ii} c_{i0}^\dagger c_{i0} + U \sum_{i,v} a_{i0}^\dagger \langle n_{i-0} \rangle c_{i0}^\dagger c_{i0} \quad (4.14)$$

Transferring back to the operators  $c_{i0}^\dagger, c_{i0}$

$$H_{HF} = \sum_i \sum_v (E_k + U n_{-v}) c_{i0}^\dagger c_{i0} \quad (4.15)$$

This is simply the Hamiltonian for a collection of non-interacting electrons with a slightly modified band structure, the energy of the  $(k, \sigma)$  state now being  $(E_k + U n_{\sigma})$  rather than  $E_k$ . If  $\rho(E)$  represents the density of states per spin corresponding to the band structure  $E_k$ , then the densities of state  $\rho_{\sigma}(E)$  where  $\sigma = \uparrow, \downarrow$  for the electrons described by the Hamiltonian of (4.13) are

$$\rho_{\sigma}(E) = \rho(E - U n_{\sigma}) = \rho(E - U n + U n_{\sigma}) \quad (4.16)$$

where the last term follows from

$$n_{\uparrow} + n_{\downarrow} = n \quad (4.17)$$

If  $\mu$  is the chemical potential of the electrons then at the absolute zero of temperature, one has

$$n_{\sigma} = \int_{-\infty}^{\mu} \rho_{\sigma}(E) dE = \int_{-\infty}^{\mu} \rho(E - U n + U n_{\sigma}) dE \quad (4.18)$$

The pair of equations (4.18) must now be solved together with (4.17) for  $n_{\uparrow}$ ,  $n_{\downarrow}$  and  $\mu$ .

One possible solution of equation (4.18) is when

$$n_{\uparrow} = n_{\downarrow} = n/2 \quad (4.19)$$

which represents a non magnetic state of the system :  $\mu$  is determined by

$$n/2 = \int_{-\infty}^{\mu} \phi(E) dE - \frac{1}{2} \int_{-\infty}^{\mu} \psi(E) dE \quad (4.20)$$

It may be possible to find ferromagnetic solution even if  $n_1 \neq n_2$  provided  $U$  is sufficiently large. In this case equations (4.18) must have two distinct solutions such that they satisfy equation (4.17).

It can be readily seen that the condition (4.19) and (4.20) give a double solution of (4.18). But this condition can at once be found from (4.18) to be

$$1 = U \int_{-\infty}^{\mu} \phi(E) dE \quad (4.21)$$

Thus, if for any  $E$ , the condition  $U \int_{-\infty}^{\mu} \phi(E) dE > 1$  is satisfied, then for some  $\mu$  and  $\mu$  determined by (4.20) and (4.21) Hartree-Fock theory predicts that the system will become ferromagnetic. It will be found that when correlation effects are taken into account one obtains a somewhat more restrictive condition for ferromagnetism.

#### 4.4 SEA AND CLUSTER SEA ADAPTED TO FERROMAGNETIC ALLOYS

In an alloy  $A_xB_{1-x}$  having atoms A and B distributed in a random manner, the Hamiltonian is given by

$$H = \sum_i \epsilon_i \sigma_i^\dagger \sigma_i + \sum_{\langle i,j \rangle} V_{ij} \sigma_i^\dagger \sigma_j + \sum_i U_i \sigma_i^\dagger \sigma_i \sigma_i^\dagger \sigma_i \quad (4.22)$$

where  $\sigma_i^\dagger = \sigma_{i\sigma}^\dagger$  are the creation and annihilation operators respectively of an electron with spin  $\sigma = (\uparrow \text{ or } \downarrow)$  of the Wannier orbital at the  $i^{\text{th}}$  lattice site.  $\epsilon_i$  is the average energy of an electron at the  $i^{\text{th}}$  lattice site taking values  $\epsilon_A$  and  $\epsilon_B$  depending upon whether A atom or B atom occupies the  $i^{\text{th}}$  lattice site.  $V_{ij}$  is the second term represents the transfer integral between the sites i and j which we assume to be independent of the species of atoms occupying these sites.  $U_i$  is the last term is the Coulomb integral of the electrons, taking values  $U_A$  or  $U_B$  depending on the atoms on the  $i^{\text{th}}$  lattice sites. We assume that the parameters  $\epsilon_A$ ,  $\epsilon_B$ ,  $V_{ij}$ ,  $U_A$  and  $U_B$  are independent of the concentration of the given alloy  $A_xB_{1-x}$ .

The Hamiltonian (4.22) is an adaptation of the Hamiltonian proposed by Falicki et al (1988) to ferromagnetic alloys for a single band model. The Coulomb interaction term introduced in the Hamiltonian following the model assumed by

Hubbard (1963) and Korshak (1963) in their discussions of the electron correlation. The assumption of non-randomness of the  $V_{ij}$  means that the band shape is very small & is the same as that in pure metal  $\delta$ . For the alloys, having the transition metals as their constituents, the Hamiltonian given by (4.22) will represent the essential aspects of the electronic structure. Besides the Hamiltonian is the simplest among the conceivable models.

Using the Hartree-Fock approximation discussed in the earlier chapter, we write the effective Hamiltonian  $\bar{H}_0$  for electrons with spin  $\sigma$  as

$$\bar{H}_0 = \sum_i \epsilon_{i\sigma} a_{i\sigma}^\dagger a_{i\sigma} + \sum_{ij} V_{ij} a_{i\sigma}^\dagger a_{j\sigma} \quad (4.23)$$

$$\text{where } \epsilon_{i\sigma} = \epsilon_i + \frac{1}{N} \langle a_{i-\sigma}^\dagger a_{i-\sigma} \rangle \quad (4.24)$$

where  $\langle a_{i-\sigma}^\dagger a_{i-\sigma} \rangle = n_{i-\sigma}$  is the average number of electrons with spin  $-\sigma$  at the  $i^{\text{th}}$  lattice site. The average number will be given by

$$\langle a_{i-\sigma}^\dagger a_{i-\sigma} \rangle = n_{i-\sigma} \quad (4.25)$$

where  $i = A$  or  $B$ .

In a realistic model we should consider a multi-band case. rather than the single band case we have

been discussing so far. In this case, the one electron Hamiltonian for the given alloy is assumed to have the form

$$H = \sum_{i,j\in\Omega} \epsilon_{ij\sigma} a_{ij\sigma}^{\dagger} a_{ij\sigma} + U \quad (4.26)$$

$$\text{with, } \epsilon_{ij\sigma} = \epsilon_1 + U_{ij} \langle a_{i\sigma\sigma}^{\dagger} a_{j\sigma\sigma} \rangle$$

$$\begin{aligned} & + \sum_{\sigma' \in \langle \sigma \rangle} U_{ij\sigma'} \langle a_{i\sigma'}^{\dagger} a_{j\sigma'} \rangle \\ & - \sum_{\sigma' \in \langle \sigma \rangle} J_{ij\sigma'} \langle a_{i\sigma'}^{\dagger} a_{j\sigma'} \rangle \end{aligned} \quad (4.27)$$

where  $\sigma$  stands for one of the degenerate bands and the corresponding atomic orbital. Other subscripts are the same as in the case of nondegenerate band.  $U_{ij\sigma}$  and  $J_{ij\sigma}$  are the on site Coulomb and exchange integrals between different orbitals labelled by  $i$  and  $j$ . We represent that part of the Hamiltonian which gives rise to the state density  $\rho^{\sigma\sigma}(x)$  for all  $\sigma$  and  $x$ . For simplicity we assume that the Coulomb integrals are the same for all  $i$ ,  $j$  and  $\sigma$  i.e.  $U_{ij\sigma\sigma'} = U_{ij\sigma} = U$  and similarly the exchange integrals between different orbitals are of the same magnitude  $J_{ij\sigma\sigma'} = J$ . We assume that  $\epsilon_{i\sigma} = \langle a_{i\sigma\sigma}^{\dagger} a_{i\sigma\sigma} \rangle$  is the same for all  $\sigma$ .  $\epsilon_{ij\sigma}$  which is now independent of  $\sigma$  is given by



$$\begin{aligned}
\epsilon_{\text{band}} = \epsilon_{\text{ion}} = \epsilon_L + U n_{L=0} = \sum_{\sigma \in \{ \uparrow, \downarrow \}} U n_{L\sigma, l=0} + \sum_{\sigma \in \{ \uparrow, \downarrow \}} \epsilon n_{L\sigma, l=0} \\
= \sum_{\sigma \in \{ \uparrow, \downarrow \}} J n_{L\sigma, l=0}
\end{aligned}$$

$$= \epsilon_L + U n_{L=\uparrow} + 4 \epsilon n_{L=\uparrow} + 4 U n_{L=\downarrow} + 4 \epsilon n_{L=\downarrow}$$

$$= \epsilon_L + 5U n_{L=\uparrow} + 4 (U+\epsilon) n_{L=\downarrow}$$

$$= \epsilon_L + 5U n_{L=\uparrow} + 4 (U+\epsilon)(n-n_{L=\uparrow})$$

$$= \epsilon_L + 5U n_{L=\uparrow} - 4(U+\epsilon)n_{L=\uparrow} + 4(U+\epsilon)n$$

$$= \epsilon_L + U n_{L=\uparrow} + 4 \epsilon n_{L=\uparrow} + \text{Const}$$

(redifining the zero of the energy again)

$$= \epsilon_L + (U+4\epsilon) n_{L=\uparrow} \quad (4.28)$$

In the coherent potential approximation the average number of electrons at a site does not depend on the site, though it depends on the species of atom occupying the site. The average numbers  $n_{A\sigma}$  or  $n_{B\sigma}$  will be calculated self consistently by the use of the formula given below.

In our problem, the coherent potential is spin dependent and so it will be represented by  $\epsilon_{\sigma}$ . While  $\epsilon_L$  and  $\epsilon_B$  are replaced by  $\epsilon_{A\sigma}$  and  $\epsilon_{B\sigma}$  to obtain the necessary formulas from Valucký et al (1988) paper. Then the coherent potential  $\epsilon_{\sigma}$  which is a function of  $z$  where  $z = x + 5\theta$  should satisfy for a given concentration  $x$  and  $1-\phi$

$$n = x_{A0} + (1-x) x_{B0} = x_{A0} \quad (4.1)$$

$$= [x_{A0} - x_{A0}(x) G_{A0}(x)] [x_{B0} - x_{B0}(x) G_{B0}(x)] \quad (4.22)$$

where  $G_{\alpha}(x)$  is given by

$$G_{\alpha}(x) = G^{(0)}(x - x_{\alpha}(x)) \\ = \int_{-\infty}^{\infty} \frac{\rho^{(0)}(x')}{x - x_{\alpha}(x) - x'} dx' \quad (4.23)$$

where  $\rho^{(0)}(x)$  is the density of states per unit energy defined for the energy band given by the second term in the right hand side of the equations (4.22) and (4.23). The average number of electrons on the atom A or B is calculated by the relation

$$n_{1\alpha} = \int_{-\infty}^{\infty} \rho_{1\alpha}(x) f(x) dx \quad (4.24)$$

where  $\alpha = A$  or B

where  $f(x)$  is the Fermi distribution function at a given temperature  $T$ ,

$$f(x) = \frac{1}{1 + \exp \{ (x - \mu) / kT \}} \quad (4.25)$$

$\rho_{1\sigma}(x)$  is the energy distribution function of electrons on atom 1 given by

$$\rho_{1\sigma}(x) = -\frac{1}{\pi} \operatorname{Im} \left[ \frac{\langle \hat{Q}_{1\sigma}(x) \rangle}{(1 - \langle \hat{Q}_{1\sigma}(x) \rangle - \hat{\Sigma}_{1\sigma}(x)) \langle \hat{Q}_{1\sigma}(x) \rangle} \right] \quad (4.33)$$

$$\text{where } x \rightarrow x + i\delta$$

In the case of COFA, we embed a cluster of atoms in the effective medium. We demand, that there is no extra scattering on the average as a result. As in ICFA, we find the self energy  $\hat{\Sigma}$  self-consistently. In COFA, however,  $\hat{\Sigma}$  will be a matrix with components between sites within the cluster. Having self-consistently calculated  $\hat{\Sigma}$  and also the configurationally averaged Green function for both up and down cases, the partial density of states  $\rho_{1\sigma}(x)$  will be given as

$$\rho_{1\sigma}^{\pm}(x) = -\frac{1}{\pi} \operatorname{Im} \left[ \frac{\langle \hat{Q}_{1\sigma}^{\pm}(x) \rangle}{(1 - \langle \hat{Q}_{1\sigma}^{\pm}(x) \rangle - \hat{\Sigma}_{1\sigma}^{\pm}(x)) \langle \hat{Q}_{1\sigma}^{\pm}(x) \rangle} \right] \quad (4.33a)$$

$$1 = A \text{ or } B$$

$$x \rightarrow x + i\delta$$

For the ICFA,  $\hat{\Sigma}$  has two independent elements  $\Sigma_0$  and  $\Sigma_1$ , one diagonal and the other off-diagonal. The self-energies are determined self-consistently within the augmented space formalism discussed in Chapter II.

For practical calculations we select parameters

$\epsilon_A, \epsilon_B, U_A, U_B$  and the state density function  $\rho^{\text{tot}}(\epsilon)$  as the input. We determine six unknown quantities  $n_{A\sigma}$  ( $i = A$  or  $B$ ) and  $\sigma = \uparrow$  or  $\downarrow$  and  $\bar{S}_G$  through six simultaneous transcendental equations.

After solving the simultaneous equations (4.25) to (4.28) we obtain various physical quantities of the alloy. The density of states of electrons with spin  $\sigma$  is

$$\rho_{\sigma} = c \rho_{A\sigma} + (1-c) \rho_{B\sigma} \quad (4.29)$$

The average number of electrons with spin  $\sigma$  per atom is given by

$$n_{\sigma} = c n_{A\sigma} + (1-c) n_{B\sigma} \quad (4.30)$$

The magnetic moment of A or B atom in the units of  $\mu_B$  is obtained by

$$m_i = 5 (n_{i\uparrow} - n_{i\downarrow}) \quad (4.31)$$

( $i = A$  or  $B$ )

the factor 5 accounts for the five fold degeneracy of the actual d-bands. The average magnetic moment of the alloy per atom in the same unit is given by

$$m = c m_A + (1-c) m_B \quad (4.32)$$

There are, as usual, two nested self-consistency loops. With a given choice for  $\epsilon_{L\sigma}$  we fix our  $\epsilon_{U\sigma}$  and carry out the CPA calculation for the averaged Green functions  $\langle G_{\sigma}(z) \rangle$  as described in Chapter II. This involves a self-consistent evaluation of  $\Sigma_{\sigma}$ . Then we recalculate  $\epsilon_{L\sigma}$  and  $\nu$  using (4.21) and then iterate till self-consistency is achieved.

We should note that we have set out to generalize the augmented space approach to cases which require a self-consistent determination of the Hamiltonian. We have achieved this in this section in its application to a simple model. The final object will be to demonstrate an actual implementation of this to a canonical example.

#### 4.5 APPLICATION TO $Si_{1-x}Fe_x$ SYSTEMS

In our calculation, we require  $\rho^{(0)}(z)$  as an input. Hasegawa and Kasamori (1971) has taken a step-like model. We, however, take as our input the realistic density of states obtained from the recursion method as described in Chapter III. We have already described this calculation in the earlier chapter in some detail. This input is quantitatively far superior to the step-like model.

We will take, for pure nickel, 1.00 electrons per

atom per d-band and in pure iron 1.44 electrons per atom per d-band. In order to reduce the adjustable parameters, we will assume  $U_1 = U_2 = U$ . The  $U$  value is also adjustable. Hasegawa and Kanamori (1971) have taken  $U = 1.25$  in units of a half of the band width of the pure metal. We have, however, in our multi band case, taken  $U$  to be 0.5 and  $J = 0.15$  so that  $(U+J)$  which approximately corresponds to  $U$  in the non degenerate case is equal to 1.25, which is very nearly equal to Hasegawa and Kanamori's  $U = 1.25$ . In our case (degenerate bands),  $\rho_{1\sigma}$  depends upon both  $n_{1\sigma}$  and  $n_{1-\sigma}$  unlike the degenerate case where  $\rho_{1\sigma}$  depends on  $n_{1-\sigma}$  only. So long as  $n_{1\sigma}n_{1-\sigma}$  is kept constant this will introduce no greater difficulties.

In the practical calculation, we first start with appropriate guess values of  $\rho_{1\sigma} = \rho_{2\sigma}$ ,  $\rho_{1-\sigma} = \rho_{2-\sigma}$ . With the help of equation (4.28) and (4.30), we self consistently find the value of  $\langle C_{1\sigma}^\dagger \rangle$  and  $\langle C_{1\sigma} \rangle$ . Knowing these, we can calculate  $\rho_{1\sigma}$ 's and the corresponding  $n_{1\sigma}$ 's. The trial values of  $n_{1\sigma}$ 's which were used in the calculation of  $\rho_{1\sigma}$ 's should be very near  $n_{1\sigma}$ 's thus calculated. The whole cycle of computation is iterated until the consistency between the trial values and calculated values of  $n_{1\sigma}$ 's are within a prechosen error bar. Knowing  $n_{1\sigma}$ 's, we proceed to find  $\rho_{\sigma}$ , the density of states with spin  $\sigma$ ,  $n_{\sigma}$  the number of electrons with spin  $\sigma$ , the magnetic moment  $M_1$  of the 1<sup>st</sup> atom ( $i = A$  or

5) and finally 6, the average magnetic moment of the alloy via equations (4.34) to equations (4.37) respectively.

Note that while the band centres for Ni and Fe are being self-consistently calculated, the band centre of Ni is kept effectively at zero for both up and down cases. The centre for Fe is correspondingly shifted. The  $\epsilon_{\sigma}^{\uparrow}(\epsilon)$ s and  $\epsilon_{\sigma}^{\downarrow}(\epsilon)$ s for various energy values are calculated. The  $n_{\sigma}^{\uparrow}$ 's are calculated after shifting the band centres back to their original positions. Also, due consideration is taken regarding the difference of the band centre for pure Ni in up and down cases. The component densities of states for both up and down cases are checked for normalization. The magnetic moment calculations can be done only with the properly normalized density of states.

#### 4.6 RESULTS AND DISCUSSION

Figures (4.1) and (4.2) show respectively the density of states per spin per unit energy for various concentrations of Fe in CPA and GCPA. It is obvious from the figures (4.1) and (4.2) that for both CPA and GCPA the minority spin band (or down spin band) deforms itself considerably, whereas the majority spin band (or up spin band) more or less keeps its shape intact with changing concentrations of Fe in the alloy. Expectedly, in the GCPA

CPA COMPONENT DOS  
 $M = 90\%$ ,  $Pd = 10\%$

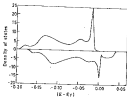


Fig. 4.1a Energy against component densities of states in CPA for  $c = 0.1$

CPA COMPONENT DOS  
 $M = 85\%$ ,  $Pd = 15\%$

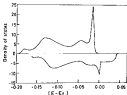


Fig. 4.1b Energy against component densities of states in CPA for  $c = 0.15$



## CPA DENSITY OF STATES

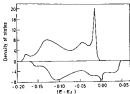
 $P_0 = 20\%$ 

Fig. 4.10 Energy against component densities of states in CPA for  $\alpha = 0.20$

## CPA DENSITY OF STATES

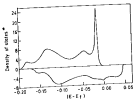
 $P_0 = 25\%$ 

Fig. 4.10 Energy against component densities of states in CPA for  $\alpha = 0.25$

Fe = 30%

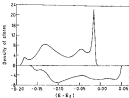


Fig. 4.1a Energy against component densities of states in CPA for  $\alpha = 0.30$

CPA COMPONENT DOS  
Fe = 30%, Fe = 10%

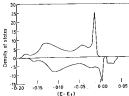


Fig. 4.2a Energy against component densities of states in CPA for  $\alpha = 0.10$

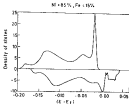


Fig. 4.2b Energy against component densities of states in CCPs for  $\alpha = 0.15$

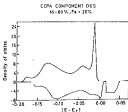


Fig. 4.2a Energy against component densities of states in CCPs for  $\alpha = 0.20$

CCPA COMPONENT DOS  
 H=70%, Fe=30%

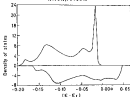


Fig. 4.24 Energy against component densities of states in CCPA for  $c = 0.25$

CCPA COMPONENT DOS  
 H=70%, Fe=30%

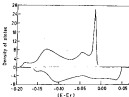


Fig. 4.25 Energy against component densities of states in CCPA for  $c = 0.30$

(Fig 4.2), there are more structures in the down spin band. In both up and the down spin bands, we have a sharp peak in the vicinity of the Fermi level (towards the immediate left of the Fermi level in the up spin band and towards the immediate right of it in the down spin band.)

The deformation in the minority spin bands for various Fe concentrations in the alloy are due to the fact that the band centres of Ni and Fe are further apart in the minority spin bands than in the majority spin case where the band centres are very close to each other. The band centres of Ni and Fe for both up and down spins, can also be calculated from equation (4.26) provided the electron numbers for Ni and Fe for various concentrations of Fe are known. Hasegawa & Kanemori [1971] have given estimates of these quantities which they have used for their work.

Apart from the deformation in the minority spin band, another feature observed in Figures (4.1) and (4.2) is that the peak observed in the minority spin band (on the right of Fermi level) gets widened with increasing concentration of Fe in the alloy. Also its height decreases gradually till the peak almost disappears into a shoulder at 50% of Fe concentration in the alloy. This is observed both in CPA as well as in GCPA. In the latter case, a impurity

subband appears in the minority band. The CPA already indicated the beginnings of the subband splitting off. This subband merged into the minority band as the concentration of Fe increased to 15%.

In Figures (4.3) and (4.4) we show the energy distribution of electrons at Ni and Fe sites (the partial densities of states)  $\rho_{\text{Ni}}(E)$  and  $\rho_{\text{Fe}}(E)$  for various Fe concentrations in CPA case. Figures (4.5) and (4.6) are their equivalents in the OCPA. Again, as in the case of component densities of states, the partial densities of states for both Fe and Ni in the majority spin state preserve their shape for various Fe concentrations, to such an extent that the partial densities of states for Fe and Ni at any concentration of Fe tally with one another so that they could not be shown distinctly in one figure. This, however, was not so in the minority spin states, where, even for a particular concentration of Fe in the alloy, Fe and Ni have very different shapes.

Another noticeable feature is that in the case of Ni, the peaks (corresponding to the two cases of spin up and spin down) are very close to each other on either side of the Fermi level. In the case of Fe, however, the corresponding peaks are separated by larger energy gaps. Also, unlike the case of partial density of states for Ni, in that for Fe, the

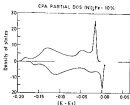


Fig. 4.7a Energy against partial density of states of Ni in CPA for  $\alpha = 0.10$

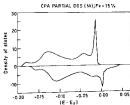


Fig. 4.7b Energy against partial density of states of Mn in CPA for  $\alpha = 0.15$

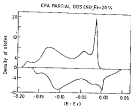


Fig. 4.3a Energy against partial densities of states of Ni in CPA for  $c = 0.20$

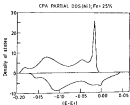


Fig. 4.3b Energy against partial densities of states of Ni in CPA for  $c = 0.25$



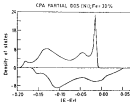


Fig. 4.3a Energy against partial densities of states of Fe in CPA for  $c = 0.10$

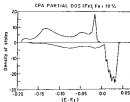


Fig. 4.4a Energy against partial densities of states of Fe in CPA for  $c = 0.10$

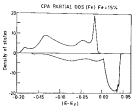


Fig. 4.4b Energy against partial density of states of Fe in CPA for  $c = 0.15$

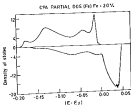


Fig. 4.4c Energy against partial density of states of Fe in CPA for  $c = 0.20$

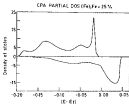


Fig. 4.4d Energy against partial densities of states of Fe in CPA for  $c = 0.25$

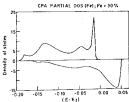


Fig. 4.4e Energy against partial densities of states of Fe in CPA for  $c = 0.50$

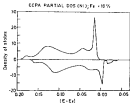


Fig. 4.5a Energy against partial densities of states of Ni in CCPA for  $x = 0.10$

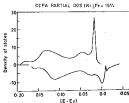


Fig. 4.5b Energy against partial densities of states of Ni in CCPA for  $x = 0.10$

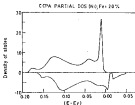


Fig. 4.5c Energy against partial densities of states of Ni in CCPA for  $c = 0.25$

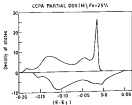


Fig. 4.5d Energy against partial densities of states of Ni in CCPA for  $c = 0.25$

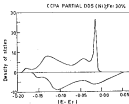


Fig. 4.5a Energy against partial densities of states of Ni in CCFA for  $c = 0.30$

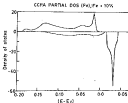


Fig. 4.5b Energy against partial densities of states of Fe in CCFA for  $c = 0.10$

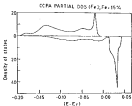


Fig. 4.6c Energy against partial densities of states of Fe in CCPA for  $c = 0.10$

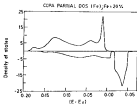


Fig. 4.6c Energy against partial densities of states of Fe in CCPA for  $c = 0.33$

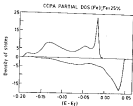


Fig. 4.5d Energy against partial densities of states of Fe in CCPA for  $\eta = 0.25$ .

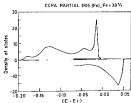


Fig. 4.5e Energy against partial densities of states of Fe in CCPA for  $\eta = 0.35$ .



peak corresponding to the spin down case is higher than that in the spin up case with increasing concentration of Fe in the alloy. For both Ni and Fe partial densities of states, the peak in the spin down case is less sharp and more spread out. Both for the CPA and CCPA the peak corresponding to up spin band has greater height than that corresponding to the down spin band in the case of Ni. This, however, is not so in the case of Fe, where for lower concentrations, the peak corresponding to the down spin band is higher in magnitude. Beyond 20%, however, even in the case of Fe, the up spin band has a higher peak than the down spin band. A comparative study of figures (4.3) - (4.6) will reveal that CPA and CCPA differ mostly in the minority spin band of Fe. This is expected since the disorder parameter  $(x_A - x_B)/M$  (where  $M$  is the band width) is large in the minority spin band. It is well known from earlier work on model systems that almost all the difference between CPA and CCPA arises in this regime. The effect is largest at low concentrations.

In the CPA calculations, magnetic moment of Fe in the alloy decreases from  $3.95 \mu_B$  at  $c = 0.1$  to  $2.60 \mu_B$  at  $c = 0.3$ , while the magnetic moment of Ni ranges from  $0.545 \mu_B$  at  $c = 0.1$  to  $0.60$  at  $c = 0.3$ . In CCPA calculations, the magnetic moment of Fe ranges from  $3.0 \mu_B$  at  $c = 0.1$  to  $2.70 \mu_B$  at  $c = 0.3$ , while that of Ni ranges from  $0.54 \mu_B$  at  $c = 0.1$  to  $0.59 \mu_B$  at  $c = 0.3$ . Figures (4.7) and (4.8) show

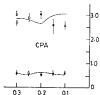


Fig. 4.7 Concentration against the magnetic moment of Ni and Fe with the experimental data by neutron diffraction (open circle by Shull and Wilkinson 1955; triangles by Collins and Low 1963; and solid circles by Kishida et al 1974).



Fig. 4.8 Concentration against the magnetic moment of Ni and Fe with the experimental data by neutron diffraction (open circle by Shull and Wilkinson 1955; triangles by Collins and Low 1963; and solid circles by Kishida et al 1974).

respectively the CPA and GCPA results of magnetic moment calculations together with the experimental results of Skull and Milkineas (1955), Collins, Jones and Loebe (1957) and Lee and Collins (1958).

It is found that the concentration dependence of the magnetic moment calculations are in good agreement with the experimental results. The agreement is particularly good for magnetic moments of Fe in the alloy at lower concentrations of Fe. Our results are an improvement over the earlier results of Hasegawa & Kanamori (1951). It is difficult to assess the relative importance of taking a more realistic density of states as compared to the simple model and the generalization of the CPA to the GCPA. Since the magnetic moment is an integrated quantity, it is difficult to estimate the effect of improvements on the density of states. In GCPA we take more than one atom into the consideration. In magnetic moments calculation therefore, GCPA should yield better results as the nearest neighbours of an atom play an important part in determining its magnetic moment. This is particularly so for Ni.

## CHAPTER V

### CONCLUDING REMARKS

In this work we have carried out the application of the Augmented Space Formalism (ASF) to study the spin fluctuations and moment formation in the case of Ni rich  $\text{Ni}_{1-x}\text{Fe}_x$  alloys, particularly for low concentrations of Fe. Previous theoretical works show larger discrepancy between the experimental and theoretical values for low concentrations of Fe in the  $\text{Ni}_{1-x}\text{Fe}_x$  alloy. Thus we have extended the Augmented Space Formalism to the case where the potential itself is calculated self-consistently. Till now the ASF was applied to parameterized Hamiltonians only with great success. In this work, however, we show that in conjunction with recursion method, the Augmented Space Formalism is a generalized method to deal with Hamiltonians which need potentials to be evaluated iteratively.

We have taken the input density of states for the exact d-bands of Ni from the recursion method. This is facilitated by the significant numerical developments made recently in this area. Haydock and Fox (1988) have devised

suitable terminator schemes for the Green function for realistic d-band density of states for the host (Si in the present case). This gives much better input than in some previous works where the atomic model was used.

In this work, we have also gone beyond the single site approximation. Apart from CPA we have also done calculations for the GCPA. As we go beyond the single site approximation the magnetic moment calculations expectedly improve. Hightings were expressed with regard to magnetic moment calculation via the coherent potential approximation. It was argued that magnetic state of a given atom depends sensitively on the composition of its nearest neighbors. So CPA as a tool for magnetic moment calculation was considered inadequate as it considers single atom with its environment treated as a mean field. GCPA, therefore, expectedly should improve results, because there we at least consider an atom and its immediate environment explicitly and replace the further away environment by a mean field.

Hasegawa and Kanamori (1972) argue that CPA is a meaningful tool for going into the details of the calculation. When the majority spin band lies below the Fermi level (as is the case of Ni), the magnetic state of each atom is stable since a fluctuation in the magnitude of the magnetic moment is brought in only by a fluctuation in the number of electrons with minority spin, then the fluctuation

is generally suppressed because it is always accompanied by a change of electrostatic energy. The neutron diffraction experiment done by Collins and Lee (1963) indicate that Fe and Co as impurities in Ni may not appreciably disturb the magnetic moments of surrounding Ni atoms. Our calculations indicate that the minority spin density on Ni-sites are most appreciably affected as we go from the CPA to the GCPA. The net result on the magnetization is small, and of any significance only in the low concentration regime i.e. the so called "impurity band" regime where model calculations earlier indicated that CPA and GCPA should differ. The magnetization at low concentrations calculated by the GCPA seems to be in better agreement with experiment. We should, however, not stress too much on this, as the tight binding model calculation should indicate trends rather than really quantitatively reliable estimates.

As future works in this area, need was felt to go beyond the tight binding approximation. For metallic alloys, the self consistent KKR-CPA techniques have been developed. The KKR equations have close resemblance to the tight binding method. The diagonal  $\epsilon_i$  term in the tight binding Hamiltonian is replaced by the inverse t-matrix. The off-diagonal hopping term  $V_{ij}$  is replaced by the structure function  $V_{ij}^{sh}$ , and the Green function by the path operator.

One has to go beyond the single site approximation.

Here as if one has to consider the magnetic states of the alloy, as magnetic moment on an atom depends on its nearest neighbours. The generalisation of the Augmented Space CPA to RKK methods has recently been carried out by Mookerjee (1987).

In cases, where the basis is not countable, an embedding technique was developed by Mookerjee and Sadhan (1988) generalising the earlier work by Inglesfield (1981). It is essentially a generalisation of the partition theorem. The augmented space method then allows us to develop a CPA procedure in such cases. This work is in progress and will enable us to study systems with random distribution of extended impurities or defects.

Our calculations are at  $T=0$ . However, most experimental observations are not at  $T=0$ . So it could be interesting to study the magnetic phase diagrams with varying temperatures. This involves the calculation of the Free energy and is a much more difficult proposition.

Fe has, as we know, both bcc and fcc phases. It could be interesting to study the structural phase transitions of alloys involving Fe. This study will involve estimation of the pair potential and through this the Free energy. This work is being taken up by our group.

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